NEW HYDROGENATING CATALYSTS

URUSHIBARA CATALYSTS

by

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PREFACE

Professor Yoshiyuki Urushibara, born in 1901, was graduated from the University of Tokyo in 1926. He devoted full time to education and research at his *alma mater* until his retirement in 1962. He has held a professorship in organic chemistry since 1946.

His career as a research chemist was solidly launched when he established the idea of prototropy in glutaconic acid derivatives. This has become the embryo of the wide ranging research in organic reaction mechanisms in Japan. The main contributions of Professor Urushibara to organic chemistry must include his work on the oxygen effect (peroxide effect) on the addition of hydrogen bromide to olefins which broadened our understanding of the reaction mechanism in organic reactions. Later he became interested in the structures and reactions of steroids and published many papers on this and related subjects. The latter work, together with the study on polymorphisms of chalcones and cinnamic acids, may, in fact, represent the dawn of the idea of conformations in this country.

It was in context of research on steroids that the Urushibara nickel catalysts, new hydrogenating catalysts, were discovered in 1951. They were soon developed for use in a variety of ways, and it is now very possible that they may replace the well-known Raney nickel catalysts. The Urushibara nickel catalysts are prepared by an extremely simple procedure in a short time (an hour or less). Their preparation involves precipitating fine grains of nickel metal from solutions of nickel salts by more electropositive metals—zinc or aluminum, and then digesting them with acid or alkali. In spite of the ease with which the catalysts are prepared, they exhibit high activity comparable to the Raney nickel catalysts. They may be effectively used for the hydrogenation and reduction of numerous organic compounds. They may also be applied to catalytic dehydrogenation, reductive desulfurization and reductive alkylation, and they may prove to be as active as the Raney catalysts. Urushibara cobalt, copper and iron catalysts have also been developed in line with the corresponding Raney catalysts. The Urushibara iron catalyst was found to be an excellent

catalyst for partial hydrogenation of acetylenic compounds to *cis*-olefins.

The progress of the investigation, and varieties of the Urushibara catalysts and their characteristics are presented in the first three chapters. Detailed descriptions of the methods of preparing each Urushibara catalyst are described in Chapter 4.

The ensuing chapters introduce the results of the investigation in connection with the nature and activities of the Urushibara catalysts. "Precipitated metals" which are deposited on particles of zinc or aluminum by an ion-exchange reaction have no catalytic activity for ordinary hydrogenation by themselves, but acquire it when digested with acids or alkalis. The question of why the "precipitated metals" are endowed with catalytic activity by acid- or alkali-treatment is discussed with reference to powder X-ray diffraction studies. Further questions whose answers are thoroughly examined include: What is the scope of activities of the Urushibara catalysts? What factors are responsible for variation in their activity?

The final chapters review and illustrate the applications of the Urushibara catalysts. It is seen that they can be applied to every kind of hydrogenation, covering not only hydrogenation in the liquid phase but also in the vapor phase. Each Urushibara catalyst has its own characteristics, and the proper choice of catalyst and appropriate reaction conditions will lead to the intended reaction. Some selective reductions and partial reductions were accomplished in this way. The last chapter includes twenty-one tables in which the comprehensive results of catalytic reactions of many sorts of compounds in the presence of the Urushibara catalysts are summarized.

Appendix chapter deals with the catalytic reactions in the presence of "precipitated metals" which had recently been found to act as catalyst by themselves under some particular conditions.

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NEW HYDROGENATING CATALYSTS

1. Introduction

Urushibara catalysts are new hydrogenating catalysts, discovered in 1951 by Y. Urushibara and his colleagues. We have at the present time four kinds of Urushibara catalysts: Urushibara nickel, Urushibara cobalt, Urushibara copper, and Urushibara iron, of which the first is to be most thoroughly discussed in the present work. These catalysts are prepared by an extremely simple procedure: fine metal particles, which are expected to manifest catalytic activity, are precipitated from solutions of their respective metal salts by more electropositive metals, and are digested with alkalis or acids. In spite of the ease with which the catalysts are prepared they exhibit high activities, comparable to those of Raney catalysts, and it seems rather strange that catalysts of such general use should have been left undiscovered until so recently.

It was due to the brilliant research of P. Sabatier around the end of the last century that catalytic hydrogenation became one of the most practical experimental tools of the organic chemist. In 1897 Sabatier hydrogenated ethylene in the presence of "reduced nickel", which was obtained by the reduction of nickel oxide in a hydrogen gas atmosphere, and in 1901 he also succeeded in obtaining cyclohexane by the addition of hydrogen to benzene in the vapor phase. This success was followed by the astonishing development of the vapor-phase catalytic reduction of many organic compounds, promising at the same time the continuing establishment of the Sabatier-Senderens method.

It was not long before catalytic reduction in the presence of a metal catalyst was applied to liquid-phase reduction as well. In 1904 C. Paal described a method for the catalytic reduction of organic compounds at ordinary temperature and pressure in the presence of colloidal platinum or colloidal palladium. Immediately thereafter the method was improved by S. Fokin, R. Willstätter, A. Skita, and others, and various preparative methods for catalysts were also introduced and generalized.

Catalysts for liquid-phase reduction under atmospheric pressure were not promising at first, however, because of their being limited to noble metals, and their preparations being so complicated. Sabatier's

" reduced nickel catalyst " had too low an activity to be used in liquid-phase reduction at ordinary temperatures. Therefore, high temperature and pressure were introduced into liquid-phase catalytic reduction in the presence of a nickel catalyst. V. N. Ipatieff exploited high pressure catalytic reduction in a cast steel autoclave, thus providing an efficient and convenient method of catalytic reduction with inexpensive catalysts such as nickel, copper, and the like.

Along with the improvement in apparatus and method of reduction, attention was being focussed on the preparation of catalysts and their activities. Many kinds of metals, single or mixed, were tested, and preparative methods were improved. In this way, many excellent catalysts of high activity were successively produced. One can quote, for example, the platinum oxide catalyst of R. Adams (1922), the nickel skeleton catalyst of M. Raney (1925), and the copper chromite catalyst of H. Adkins (1932).

Thus catalytic reduction has become one of the most important tools in chemical laboratories. Catalysts have also begun to be used in the chemical industry, where great success has been achieved in the use of catalysts, that is one of the most distinguishing characteristics of today's chemical industry. Not only hydrogenation, but also oxidation, dehydrogenation, polymerization, and condensation are effected in the presence of catalysts, and the discovery and use of new catalysts is, in both the academic and practical sense, a very important challenge to the world's chemists and chemical engineers. Discovery of a new catalyst may permit a new reaction, which would otherwise be impossible, and sometimes may lead to the establishment of a new division of synthetic chemistry. Therefore, continual effort is being made toward the discovery of new catalysts. For instance, one can mention the Ziegler catalyst as such a revolutionary new catalyst.

In such a golden age of catalytic chemistry, the circumstances which led to the discovery of Urushibara catalysts were quite peculiar. The catalysts mentioned above were discovered mainly by chemists who were investigating catalytic reactions. Urushibara catalysts, on the other hand, were not discovered as the result of research in an unknown field of catalytic chemistry, in an effort to find a new catalyst. Nor were they discovered by mere chance. It was a reduction experiment in steroid chemistry by Y. Urushibara and his co-workers that led to the discovery of these catalysts. The experiment itself had nothing to do with catalytic chemistry, but the unexpected suggestion was obtained that nickel and copper, which were deposited from their salt

solutions by more electropositive metals, were likely to exhibit catalytic activity.

Catalytic chemistry, and the hydrogenating catalysts in particular, had been so extensively investigated and developed that it appeared unlikely that the catalytic activity of a nickel powder obtained by such a simple procedure could have escaped notice. In fact, results obtained in the early stages of experimentation were quite disappointing, and the catalytic activity of the precipitated nickel was anything but satisfactory. However, intensive catalytic chemical research was concentrated on the possibility that precipitated nickel might be utilized, and that a new catalyst of high activity, comparable to Raney nickel, might be established. The catalyst was given the name of the discoverer, and called the Urushibara catalyst. It was not until 1955 that this name was first employed, and at the same time an abbreviated notation, U–Ni, was proposed.[5)+]

Since the time when Sabatier applied reduced nickel to the catalytic reduction of organic compounds, many chemists produced many different kinds of nickel catalysts by various methods. Even after Raney nickel had been generally approved as the most useful catalyst and became widely used, research continued for the discovery of new nickel catalysts, or an improvement in the preparation of Raney nickel. It may then be asked: Was nickel powder precipitated by electropositive metals never tried as a catalyst? We can find some five papers which deal with attempts to use precipitated nickel as a catalyst.

L. Kahlenberg and G. J. Ritter*[1)] deposited nickel on zinc grains from a saturated solution of nickel chloride, and dried the resulting precipitate at 125°C in a hydrogen gas flow. In its presence cotton seed oil was hydrogenated at 180°C, and it was reported that hardening of the oil occurred. G. A. Richter*[2)] applied for a patent for the preparation of a nickel catalyst in which nickel metal precipitated from solution by zinc metal is ground off from the latter, and used this catalyst for hydrogenation. A British patent*[3)] awarded to I. G. Farbenindustrie A.-G. involves the precipitation of nickel, copper, or cobalt catalyst by iron, zinc, or aluminum from the salt solution of the respective metal. A note was added that if the solution is alkaline, the oxide of the electro-

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+ 1)~48) See Bibliography in the end of this volume.

*1) L. Kahlenberg and G. J. Ritter, *J. Phys. Chem.* **25**, 109 (1921).

*2) G. A. Richter, U. S. Patent 1,451,113 (Apr. 10, 1923).

*3) I. G. Farbenindustrie A.-G., British Patent 281,218 (Nov. 27, 1926).

positive metal is precipitated along with the nickel, cobalt, or copper and this, in some instances, may act as a promotor. Another British patent,*1) awarded to the same corporation, describes the precipitation of a catalytic metal, such as nickel, in the presence of an organic base or acid amide.

V. Harlay, in a relatively recent paper,*2) reduced organic compounds in the presence of a zinc-nickel couple made from excess zinc dust in an ammoniacal solution of nickel sulfate. It was observed that in some instances reduction took place more readily in caustic soda than in neutral media.

Except for that of Harlay, who seems to have been only one step away from the idea of the Urushibara nickel catalyst, the above methods involve no treatment of the precipitated nickel with alkali or acid, which is essential for the production of the Urushibara catalysts. At any rate, the catalysts described in these papers are not very active, and there are no reports of their development and utilization.

As we have just seen little attention, if any, was paid to the catalytic use of precipitated nickel which is obtainable by the very simple method previously described. The reason may be that we are too apt to think that someone must already have obtained a catalyst by such a simple procedure; or that as we are accustomed to complicated preparations of catalysts, high activity was not expected for precipitated nickel, which could be prepared so easily.

Discovery of the Urushibara nickel catalyst was a matter of good luck, due perhaps to the innocence of a chemist who had no profound knowledge of catalytic chemistry. At any rate, this new catalyst was not born from the concentration of today's advanced catalytic research, but crept out from the enormous heap of knowledge on catalysts—buried so long unnoticed because of its so simple method of preparation.

To date, the most universally employed nickel catalyst has been Raney nickel, but the alkali treatment of Raney alloy is but one of a variety of methods for producing fine metal particles. Fine particles may be produced as well by precipitation from salt solutions with more electropositive metals; Urushibara nickel is obtained by treatment of the precipitated nickel with alkali or acid. The activity of Urushibara nickel is comparable to that of Raney nickel, and it can replace Raney nickel, in most reactions. In chemical laboratories Urushibara nickel

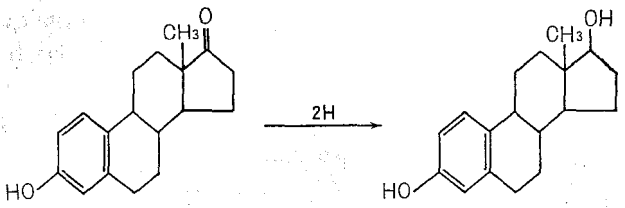
*1) I. G. Farbenindustrie A.-G., British Patent 286,123 (May 6, 1927).
*2) V. Harlay, *Compt. Rend.* **213**, 304 (1941).

is preferred, since it can be prepared far more easily than Raney nickel, the preparation of which is so troublesome, and yet the results obtained with it are by no means inferior.

2. Discovery and Development of the Urushibara Catalysts

2. 1. Discovery of the Urushibara Nickel Catalyst

It was an experiment on the reduction of estrone that led Urushibara to the discovery of the new nickel catalyst. Estrone (I) is a female hormone, which is produced on an industrial scale from the urine of pregnant mares. Its estrogenic activity increases eight- to ten-fold when converted into estradiol-17β (II) by the reduction of its carbonyl group.



(I) estrone (II) estradiol-17β

In 1933, E. Schwenk *et al.**1) of Schering A. G. applied for patents in several countries, including Japan,*2) for the reduction of estrone to estradiol. The patent covered a wide variety of chemical treatments, and almost every chemical reduction hitherto known. Later it was found that estradiol itself could be extracted from the urine of a pregnant mare, or from the ovary of a sow. The output, however, was so small that large scale industrial production necessitated the reduction of estrone, which can be obtained in large quantities as pure crystals; yet the Schering patent precluded the use of every known reduction method.

In search of a new method for reduction, Y. Urushibara and M.

*1) E. Schwenk and F. Hildebrandt, *Naturwiss.*, **21**, 177 (1933).
*2) Japanese Pat. 115,270.

Chuman noticed another patent of Schering.*[1] It described the reduction of estrone in an alkaline solution by heating with Raney alloy. In this process, the aluminum in the alloy dissolves in the alkali, releasing hydrogen, and leaves behind Raney nickel, which combines with the liberated hydrogen to reduce estrone. As reduction cannot take place when aluminum is merely added to an alkaline solution of estrone, the patent is no doubt a very ingenious device which combines Raney nickel, a powerful reducing catalyst, with the nascent hydrogen liberated by the reaction between aluminum and alkali. Many techniques were already known for the reduction of estrone by nascent hydrogen alone; they were all involved in the former patent of Schering. Considering these circumstances, Urushibara asked himself with ingenious foresight: Is it not possible that a common metal powder, not so active as Raney nickel, might reduce estrone, provided it were combined with nascent hydrogen?

The most simple procedure to obtain powdered nickel, which Urushibara intended to apply, involved precipitating nickel from a solution of its salt by adding more readily ionizable metals. By adding zinc dust to a solution of nickel chloride a nickel powder was obtained, a powder which hereafter is referred to as " precipitated nickel ". The precipitated nickel was added to an alkaline solution of estrone, and aluminum grains were then added to reduce the estrone by means of the nascent hydrogen generated, in combination with the nickel. The result was a complete success as expected, and estradiol was obtained in good yield.[3] Precipitated copper obtained in the same way from a solution of copper sulfate and zinc dust also proved to be efficient in reducing estrone to estradol.[2),27]

In this way, the first aim was achieved and a new method of reduction was established. However, Urushibara took a further step; to an alkaline solution of estrone he added precipitated nickel, and then passed hydrogen through it while shaking. This was done with only a negative expectation; for he presumed that reduction would not take place when hydrogen was merely passed through the solution without adding aluminum grains, and that the precipitated nickel or copper would be catalytically active only when combined with nascent hydrogen. To his pleased surprise, reduction took place, and estradiol was obtained. Precipitated nickel exhibited catalytic activity!

However, in the absence of alkali the above reduction failed; when

*1) Japanese Pat. 122,476.

a neutral ethanol solution of estrone was shaken with hydrogen in the presence of precipitated nickel, no reduction took place. Hence it was concluded that the precipitated nickel was catalytically active only in alkaline media.

It would not be too much to say that it was when Urushibara became interested in the effect of alkali that the chance of discovering the Urushibara catalysts themselves first appeared. The first, and perhaps most important approach to explaining the role of alkali was made by warming the precipitated nickel with caustic alkali. After this alkali treatment the precipitated nickel was washed well with water, until the wash-water was no longer alkaline. Urushibara then added the product to a neutral ethanol solution of estrone and shook it with hydrogen. In an instant, reduction took place and estradiol was obtained.

It turned out in this way that the precipitated nickel deposited from a solution of its salt by zinc dust exhibits no catalytic activity by itself, but becomes an efficient catalyst for the reduction of estrone when treated beforehand with caustic alkali. The catalyst was successively applied to many organic reductions, and many substances, such as olefins, ketones, aldehydes, and nitro compounds were effectively reduced or hydrogenated.[1),16),17)]

The activity of this catalyst was very unsatisfactory at first, and a large quantity was required to effect reduction. However it grew into a useful material, comparable to any known reduction catalyst, as investigation was concentrated on augmenting its activity and successive modifications were introduced into the preparation.[4)] The substance was then named the Urushibara nickel catalyst, subsequently abbreviated to U–Ni.[5)]

2. 2. Development of the Urushibara Catalysts

No account could be given for a long time as to why the precipitated nickel was endowed with catalytic activity when treated with caustic alkali, whereas it is devoid of activity when first precipitated. Either sodium or potassium hydroxide can be used to digest the precipitated nickel; aqueous ammonia also serves as a digesting agent, although the resulting activity is somewhat lower.

The fact that treatment of the precipitated nickel with an alkali gives rise to a highly active catalyst reminds us of the alkali treatment of the Raney nickel catalyst. Moreover, the results of the reduction of various organic compounds with Urushibara nickel are very similar to those

obtained with Raney nickel. This accidental coincidence, as it turned out later, at first led to the wrong assumptions that a trace of alkali which remained unremoved in the catalyst after alkali treatment and successive washing played an unknown but very important role in catalytic activity, and that if this were the case, the activity of Raney nickel would be attributable to the same factor.

Meanwhile, it was found that chloride ion came into solution when the precipitated nickel, washed well until the wash-water no longer gave a positive chloride test, was warmed in a sodium hydroxide solution. This led to the alternative explanation that a chlorine compound was contained in the precipitated nickel, a compound which was soluble in alkali but not in water, and which acted as a catalyst poison. The substance was concluded on the basis of X-ray diffraction studies,[13] to be zinc hydroxide chloride (basic zinc chloride), as the diffraction of the precipitated nickel exhibited peaks attributable to zinc hydroxide chloride, peaks which disappeared after alkali treatment (see 5. 2).

As for other contaminants, the precipitated nickel may contain large amounts of zinc together with zinc oxide and zinc hydroxide. Zinc, on which the nickel metal deposits, is added in excess, and zinc oxide originally contained in the zinc remains intact in the precipitated nickel. Zinc hydroxide may also be formed by the reaction between zinc and water. These contaminants are hardly removed by alkali treatment of the precipitated nickel; indeed, this procedure may conversely cause deposition of an additional amount of zinc hydroxide. Therefore the catalyst still contains the same kinds of contaminants as the precipitated nickel, a point also confirmed by X-ray diffraction studies. The high activity of the catalyst suggests that these contaminants do no harm to the activity.

If it is true that the effect of the alkali treatment of precipitated nickel to produce the Urushibara nickel catalyst is nothing but the removal of zinc hydroxide chloride, the same thing should happen when acid is used instead. The precipitated nickel was therefore warmed in dilute acetic acid, and eventually a nickel catalyst of high activity was obtained which could efficiently catalyze the reduction of many organic compounds.[5]

Propionic acid produced a somewhat better catalyst than acetic acid; but butyric acid, on the contrary, gave a poorer result. Formic acid and hydrochloric acid were ineffective.

Alkali treatment of the precipitated nickel gives rise to a catalyst of high activity due to the removal of zinc hydroxide chloride, excess zinc,

and some zinc hydroxide still remaining in the catalyst. On the other hand, acetic acid readily dissolves zinc metal, and the greatest part of the excess zinc disappears before the poisonous zinc hydroxide chloride is completely removed. When the amount of acetic acid is insufficient, the latter can not be removed completely, and moreover, zinc hydroxide acetate is formed in some instances. When this happens, catalytic activity is not found. At any rate, the removal of zinc hydroxide chloride by alkali or acid is indispensable for the activation of the precipitated nickel. The above was also confirmed by X-ray diffraction studies.

We have seen, thus far, that there were already two kinds of Urushibara nickel catalysts in the early period. The catalyst which is prepared by alkali treatment of the precipitated nickel is called " Urushibara nickel B ", and that prepared by acid treatment is called " Urushibara nickel A", abbreviated to U–Ni–B and U–Ni–A, respectively. The two catalysts differ in appearance: U–Ni–B is a dark gray power containing a large quantity of excess zinc metal, together with a greater or lesser amount of zinc oxide; whereas U–Ni–A is a black powder containing lesser amounts of zinc and zinc compounds, and 70 to 80% of its gross weight consists of nickel. U–Ni–B is by far the more bulky with respect to the total nickel content.

Both U–Ni–A and U–Ni–B were active enough for the reduction of many organic compounds, and their applications became more and more wide-spread. Moreover, as investigation proceeded, their activities increased step by step until they eventually achieved activities quite comparable to that of Raney nickel. During the early stages of investigation, Raney nickel provided a good reference standard, to which the Urushibara nickel was always compared. Dehydrogenation, reductive desulfurization, reductive alkylation, for example, were promoted as well by Urushibara nickel as they were by Raney nickel. However, hydrogenation of the benzene ring, which Raney nickel was able to promote, could not at first be effected by the Urushibara catalyst, and this was thought to be one of the defects of this new catalyst. This drawback was ultimately removed by a suggestion obtained from theoretical considerations of catalytic activity.

Many experiments and hypotheses are found in the literature which relate catalytic activity to crystal structure, electronic structure, magnetic properties, etc. We shall concern ourselves, for the moment, only with the electronic interpretation. L. Pauling*1) has pointed out that

*1) L. Pauling, *Phys. Rev.*, **54**, 899 (1938); *J. Amer. Chem. Soc.*, **69**, 5421 (1957); *Proc. Roy. Soc.*, **196**, 343 (1949).

the catalytic activity of a transition metal is affected by its *d*-electron state. D. A. Dowden*[1] has tried to single out the dominant factor influencing the catalytic activity of alloys, and discusses the contribution of electrons in the *d*-orbital. P. W. Reynold*[2] and, independently, W. W. Russel,*[3] while investigating a mixed nickel-copper catalyst, noticed that the activity of nickel gradually diminishes with the successive addition of copper, and concluded that the activity of nickel declines in parallel with the filling of the holes in its 3*d*-orbital by the valence electrons of the copper.

To return, the precipitated nickel is produced by the use of zinc metal. We have good reason to assume that the latter interacts with nickel to such an extent that the 3*d* electrons of the nickel in the Urushibara catalyst are no longer capable of hydrogenating the benzene ring. But zinc is not indispensable for the preparation of the precipitated nickel from nickel chloride solution; any metal which is more electropositive than nickel may be used instead. In the beginning, metals such as aluminum or magnesium were also employed, but zinc was afterwards used almost exclusively for the preparation of Urushibara catalysts because it was not only the most convenient agent to handle, but also gave good results. However, as far as ring hydrogenation was concerned, zinc dust, contaminating the catalyst, was found to act as a poison. It was therefore decided to try aluminum, as Urushibara nickel obtained through the use of aluminum was expected to exhibit the ability to hydrogenate benzene rings in analogy with Raney nickel, which is prepared from a nickel-aluminum alloy.

Commercial aluminum powder was too finely pulverized to allow a moderate exchange reaction to take place, and too violent a reaction rendered the preparation extremely difficult. Hence a procedure was devised in which aluminum grains of moderate size were employed to produce precipitated nickel. The precipitated nickel, subjected to treatment with caustic alkali solution, reacted as expected and effectively hydrogenated benzene rings. It was named " Urushibara nickel BA ", abbreviated to U–Ni–BA.[20] Acetic acid treatment of the nickel precipitated from nickel chloride solution by aluminum grains also gave rise to a catalyst of the same quality, which was named " Urushibara nickel AA", abbreviated to U–Ni–AA. The addition of sodium chloride or

*1) D. A. Dowden, *J. Chem. Soc.*, **1950**, 242; *Ind. Eng. Chem.*, **44**, 977 (1952).
*2) P. W. Reynolds, *J. Chem. Soc.*, **1950**, 265.
*3) W. W. Russel, *J. Amer. Chem. Soc.*, **76**, 319, 838 (1954).

other special procedures are necessary to prepare U–Ni–AA, as aluminum dissolves in acetic acid very slowly. U–Ni–AA, prepared with aluminum grains of appropriate size, contains undissolved aluminum, which in turn acts as a carrier; this is conveniently, utilized in vapor-phase reduction.[26]

In this way, a number of Urushibara nickel catalysts were developed. They were applied to the reduction of many substances, and information was rapidly accumulated. They turned out to be useful for all hydrogenations, and were active enough to be compared with Raney nickel. Not only were applications and devices explored, but also the very nature of this catalyst was energetically investigated by means of X-ray and electron diffraction. For example, it turned out that the crystal growth of nickel is more or less interrupted in the Urushibara nickel catalysts, which grow in a crystallite state; and the smaller the size of the crystallite, the more likely is the catalytic activity to be enhanced.[13]

At the same time as these physico-chemical studies were being carried out, investigations regarding the methods of preparation were also actively pushed forward. To obtain an efficient catalyst for liquid-phase hydrogenation, it was necessary to reduce the particle size of the catalyst; that is, the particle size of the precipitated nickel. The reaction between nickel chloride solution and zinc dust was carried out at room temperature or in the cold, and the precipitated nickel obtained was digested with an alkali or acid. U–Ni–B and U–Ni–A prepared in this way involved particles of smaller size, and proved to be more effective than ordinary Urushibara nickel catalysts. Urushibara catalysts prepared from metals precipitated in the cold are represented by the abbreviated notation " U–C–Catalysts ". For instance, the foregoing Urushibara nickel catalysts are called U–Ni–CB and U–Ni–CA, respectively.[34]

Though the preparation of Urushibara nickel catalysts is very straightforward, it can be rendered even more simple. For this, nickel chloride crystals, instead of their solution, are added to zinc dust mixed with a small amount of water. Urushibara nickel catalyst prepared in this way is represented as U–Ni–B(s) or U–Ni–A(s).[37] U–Ni(s) produced by this simplified method has a somewhat lower activity, but it is sufficient for practical use in ordinary hydrogenation.

Dried " precipitated nickel " may be stored for a long time in large quantities, and treatment with alkali or acid prior to use will immediately result in an Urushibara nickel catalyst of restored activity. As

Urushibara catalysts are not pyrophoric (in contrast to Raney nickel), their recovery and regeneration are very easy. To regenerate the catalyst, it is sufficient to dissolve the waste catalyst in hydrochloric acid to recover nickel chloride, from which new Urushibara nickel catalyst may be prepared. Moreover, it has been discovered that the regeneration of Urushibara nickel catalyst may be effected even more easily. Highly active U–Ni–A catalyst was regenerated when spent catalyst, even after a long period of storage, was warmed with acetic acid in either the presence or absence of a small amount of zinc dust; the regenerated catalyst proved to be as effective as freshly prepared catalyst.[36]

It sometimes happens that too high an activity brings about an unfavorable result, and it is often necessary to produce a catalyst of reduced activity. In such cases it is recommended that aqueous ammonia or hydrochloric acid be used instead of caustic alkali or acetic acid in digesting the precipitated nickel. Such catalysts of lower activity are represented as U–Ni–NH_3 or U–Ni–A(HCl), according to the digesting agent.

Investigations with regard to the Urushibara nickel catalysts gradually revealed that they resemble Raney nickel in many aspects. Raney nickel has its congeners of lower activity, such as Raney cobalt, Raney copper, and Raney iron, which, in turn, favor particular reductions. By analogy, Urushibara cobalt, Urushibara copper, and Urushibara iron were prepared successively. Urushibara cobalt is prepared according to the same method employed in the preparation of Urushibara nickel. Preparation of Urushibara copper or Urushibara iron requires special techniques. These particular Urushibara catalysts were applied to reactions which ordinary Urushibara nickel catalysts did not facilitate, and proved to be efficient for these peculiar purposes. For example, U–Co–B favors the hydrogenation of nitriles to primary amines; while the Urushibara iron catalyst, like Raney iron, has a special virtue for the partial hydrogenation of acetylenic compounds.

A very interesting observation is that the Urushibara iron catalyst prepared from iron(II) or iron(III) chloride and zinc dust exhibits a pronounced activity towards the partial hydrogenation of 2-butyne-1,4-diol, whereas U–Fe–BA catalyst, produced using aluminum grains instead of zinc dust, is entirely inactive. This evidence, together with an examination of the X-ray diffraction diagrams of the catalysts, has cast light on the problem of what is responsible for the activity of Urushibara catalysts.[39] (see Section 5. 3 below). The examination was extended over various Urushibara nickel catalysts and it was suggested

that a metal such as nickel or iron, when deposited on zinc crystals, is forced to display something like epitaxy in evaporated films, and that the change invoked in the crystal structure of the metal is the cause of the activity of the Urushibara catalysts. This hypothesis requires further experimental proof, and its validity will be the subject of future study.

3. The Various Urushibara Catalysts and Their Characteristics

3.1. Variety of Urushibara Catalysts

We have so far mentioned four kinds of Urushibara catalysts: Urushibara nickel, Urushibara cobalt, Urushibara copper, and Urushibara iron. These Urushibara catalysts are prepared by digesting with an alkali or acid the catalytic metals which are precipitated from solutions of their salts by more electropositive metals. Zinc and aluminum are most frequently employed in precipitating the catalytic metals from their solutions. Metals deposited by the ion-exchange reaction are called "precipitated metals", and are always contaminated with a certain amount of the metal used as a precipitating agent or its oxide, salts, or the like. For instance, precipitated nickel from nickel chloride solution and zinc dust contains a large amount of zinc metal, and greater or lesser amounts of zinc oxide and zinc salts.

The precipitated metals have no catalytic activity for ordinary hydrogenation by themselves, but are endowed with it when washed with water and digested with alkalis or acids. In this way, we obtain what are called the Urushibara catalysts. A variety of Urushibara catalysts can be obtained according to the method of preparation of the precipitated metals, or according to their subsequent treatment with alkalis or acids. The Urushibara catalyst prepared by treating the precipitated metal with an alkali is represented by the letter B (base), and that prepared by treating it with an acid is represented by the letter A (acid). For example, abbreviated notations such as U–Ni–B or U–Ni–A are used.

Zinc is most commonly used to precipitate the catalytic metals. Aluminum can be used instead of zinc, giving rise to catalysts of specific activity which are represented with the letter A (aluminum) added after the symbols A or B, which specify the digesting agent; thus, U–Ni–BA or U–Ni–AA.

Besides ordinary Urushibara catalysts which are prepared by standard methods, there are a number of Urushibara catalysts which are pro-

Table 3-1. Urushibara Catalysts

No.	Notation	Source of precipitated metal	Precipitating agent	Temperature of precipitation	Digesting agent	Temperature of digestion	Method of preparation[b]
1	U-Ni-B	$NiCl_2$ solution	Zn dust	high temp.	10% NaOH	50–55°C	1, 3
2[a]	U-Ni-B	$Ni(CH_3CO_2)_2$ solution	〃	〃	〃	〃	5
3	U-Ni-CB	$NiCl_2$ solution	〃	room temp. or under cooling	〃	under cooling	7
4	U-Ni-B(s)	$NiCl_2 \cdot 6H_2O$ crystals	〃	spontaneous rise of temp.	〃	50°C	10
5	U-Ni-NH_3	$NiCl_2$ solution	〃	high temp.	aq. NH_3	50–60°C	12
6	U-Ni-BA	〃	Al grains	spontaneous rise of temp. (cooling)	20% NaOH	under cooling <60°C	15, 16, 17
7[a]	U-Ni-BA	〃	Al powder	high temp.	〃	under cooling	14
8	U-Ni-A	〃	Zn dust	〃	13% AcOH	room temp. or 40°C	4
9[a]	U-Ni-A	$Ni(CH_3CO_2)_2$ solution	〃	〃	〃	〃	6
10[a]	U-Ni-A	$NiCl_2$ solution	〃	〃	20% propionic acid	50°C	4
11	U-Ni-CA	〃	〃	room temp. or under cooling	10% AcOH	under cooling with water	8
12	U-Ni-A(s)	$NiCl_2 \cdot 6H_2O$ crystals	〃	spontaneous rise of temp.	20% AcOH	room temp.	11
13	U-Ni-A (HCl)	$NiCl_2$ solution	〃	high temp.	0.75 N HCl	〃	13
14	U-Ni-A(s) (HCl)	$NiCl_2 \cdot 6H_2O$ crystals	〃	spontaneous rise of temp.	〃	〃	13
15	U-Ni-AA	$NiCl_2$ solution	Al grains	high temp.	AcOH+NaCl	70°C	18
16	U-Co-B	$CoCl_2$ solution	Zn dust	〃	10% NaOH	50–55°C	19

17	U–Co–CB	„	„	room temp. or under cooling	„	under cooling	21
18	U–Co–B(s)	$CoCl_2 \cdot 6H_2O$ crystals	„	spontaneous rise of temp.	„	moderate temp.	23
19	U–Co–A	$CoCl_2$ solution	„	high temp.	13% AcOH	room temp.	20
20	U–Co–CA	„	„	room temp. or under cooling	10% AcOH	under cooling with water	22
21	U–Co–A(s)	$CoCl_2 \cdot 6H_2O$ crystals	„	spontaneous rise of temp.	15% AcOH	room temp.	24
22	U–Co–A(s) (HCl)	„	„	„	0.75 N HCl	„	25
23	U–Co–BA	$CoCl_2$ solution	Al grains	„	20% NaOH	under cooling <60°C	26
24	U–Cu	$CuCl_2$ solution	Zn dust	high temp.	13% AcOH	70–75°C	27
25	U–Cu–C	„	„	under cooling with ice	„	room temp.	28
26[a]	U–Cu–C	„	„	„	20% AcOH	80–90°C	29
27	U–Fe(II)	$FeCl_2 \cdot 4H_2O$ crystals	„	high temp.	15% AcOH	60–70°C	31
28	U–Fe(III)	$FeCl_3 \cdot 6H_2O$ crystals	„	spontaneous rise of temp.	„	„	30
29	U–Fe(II)–Ni	$FeCl_2 \cdot 4H_2O$ crystals $NiCl_2$ solution	„	high temp.	„	„	33
30	U–Fe(III)–Ni	$FeCl_3 \cdot 6H_2O$ crystals $NiCl_2$ solution	„	spontaneous rise of temp.	„	„	32
31	U–Fe(II)–Co	$FeCl_2 \cdot 4H_2O$ crystals $CoCl_2$ solution	„	high temp.	„	„	34
32	U–Fe(III)–Co	$FeCl_3 \cdot 6H_2O$ crystals $CoCl_2$ solution	„	spontaneous rise of temp.	„	„	34
33	U–Fe(III)–BA	$FeCl_3 \cdot 6H_2O$ crystals	Al grains	spontaneous rise of temp. (cooling)	20% NaOH	under cooling	35

[a] Notations do not differ from the preceding ones. Further preparation conditions are to be added where required.

[b] Preparation numbers are described in detail in Chapter 4.

duced by somewhat modified methods. These modifications are distinguished from usual preparations by particular symbols, each of which stands for the individual modification. The letter C, as in U–Ni–CA, stands for an Urushibara catalyst prepared by a modified procedure in which an ion-exchange reaction is carried out at room temperature or in the cold, reducing the particle size to as small a size as possible. The symbol (s) is used to indicate an Urushibara catalyst prepared by a simplified method, which involves a reaction between crystals of catalytic metal salts and metals to be used for the precipitating agent, mixed with a small amount of water. Here, notation such as U–Ni–B(s) is used. Names of catalysts which are digested with aqueous ammonia or hydrochloric acid are represented by attaching the chemical formulae of the respective digesting agents, NH_3 or HCl.

The Urushibara catalysts produced up to the present day are tabulated in Table 3–1.

3. 2. General Characteristics of the Urushibara Catalysts

As we have seen in the preceding paragraph, there are many varieties of Urushibara catalyst. Of these catalysts, U–Ni–A and U–Ni–B are most frequently used, the former being by far the most important catalyst, since it is useful for almost every reduction. U–Ni–A, as well as U–Ni–A(s), serves for almost every liquid-phase hydrogenation; U–Ni–AA is especially effective for vapor-phase catalytic reductions. Other catalysts are prepared for particular purposes, and are not always efficient for all reductions.

The general characteristics common to these Urushibara catalysts are as follows:

(1) They may be used for miscellaneous reductions, such as the hydrogenation of ethylenic and acetylenic compounds and benzene rings, and the reduction of carbonyl compounds, oximes, nitriles, and nitro compounds, etc. Their activities are very similar to those of Raney catalysts. As far as the author is aware, all reductions which Raney catalysts promote are effected as well in the presence of an Urushibara catalyst, and the activities of the Urushibara catalysts are, under both ordinary and high pressures, by no means lower than displayed by Raney catalysts.

Urushibara catalysts are also used in dehydrogenation, reductive desulfurization, and reductive alkylation, and have proved to be as active for these reactions as Raney catalysts (see Chapter 8).

(2) In general, the preparations of Raney catalysts or other earlier catalysts are very involved, and require a long time. Moreover, they must be treated with great caution. On the other hand, the preparation of Urushibara catalysts is very simple and rapid. They can be prepared from commercial materials by simple operations in only an hour or less. Simple operations allow an untrained person to easily obtain catalysts of high activity.

As for U–Ni–A and U–Ni–B, it is worth noting that the more vigorous the reaction between the nickel chloride solution and the zinc dust, the more likely the activity of the catalyst will be promoted; a mild and lengthy reaction which is brought about by the gradual addition of the reagents will reduce the activity. This is one of the unique characteristics of the Urushibara catalysts.

(3) As Urushibara catalysts are not very sensitive to impurities, they can conveniently be produced from commercial chemicals of ordinary grade without careful choice. Reagents such as nickel chloride, zinc dust, aluminum, sodium hydroxide, and acetic acid may be " chemically pure " grade commercial materials. City water is sufficient for use in preparing the precipitated metals. (If, however, it contains poisoning metal ions or other poisoning materials, purified water must be used.) Purified water should be used in the digestion process.

(4) Dried precipitated metal can be stored for a long time without decreasing the activity of the catalyst which is to be prepared. The catalyst prepared from the stored precipitated metal does not differ in activity from that prepared from freshly precipitated metal. Preparation time can be greatly reduced if a large quantity of the precipitated nickel is prepared in advance from nickel chloride and zinc dust and stored; from this the requisite amount can be occasionally taken out to be digested with an acid or alkali. The time required for digestion with acid or alkali almost never exceeds twenty minutes.

(5) The handling of an Urushibara catalyst is safe and easy, as it is not inflammable upon contact with air, in contrast to Raney catalyst which is pyrophoric. Newly prepared U–Ni–A does ignite spontaneously when dried after washing with ether; however, it does not ignite when washed with methanol or ethanol and left standing wet in the air for a short time. U–Ni–B never ignites even if washed with ether and dried.

(6) Waste catalyst does not ignite when left standing after being filtered from the reaction mixture, washed with water or other solvents, and dried. Therefore, used catalyst can easily be recovered and re-

generated. For regeneration, the waste catalyst is converted to its salt, nickel chloride for example, from which a new U–Ni catalyst is produced. An alternative and simpler method for regenerating a U–Ni–A catalyst of high activity has been discovered, in which a spent catalyst is treated with acetic acid in the presence or absence of a small amount of zinc dust (see Section 6. 4. 2). The operation permits the repeated use of the catalyst.

(7) As the materials used in preparing the catalyst are inexpensive, they may be used in large quantity without much expense. In laboratory scale production one need not worry about recovery and regeneration.

(8) Urushibara catalysts preserve their activities for considerably long periods when stored carefully in a solvent free from dissolved air. Long storage, however, is not really necessary, since the catalysts can be prepared easily in a short time whenever required. For maximum convenience, therefore, storage in the state of the precipitated metal is recommended instead.

(9) The durability of the Urushibara catalyst during a reaction is not quite satisfactory; this is also the case with the Raney catalyst. This matters little in practical use, as the Urushibara catalyst is inexpensive and its preparation, recovery, and regeneration can be carried out very easily.

(10) The catalytic activities of the Urushibara catalysts with respect to a particular substance differ according to the type of catalyst. In addition, there are a few cases where the Urushibara catalyst shows a lower activity than the Raney catalyst for a particular reduction. Therefore, selective reduction can easily be programmed by choosing the catalyst or the reaction conditions. For instance, the use of the Urushibara iron catalyst particularly favors the partial hydrogenation of acetylenic compounds to ethylenes.

(11) Though Urushibara catalysts are usually employed in liquid-phase reduction under both ordinary and high pressures, they can also be used in vapor-phase reduction, provided appropriate apparatus is employed. Specifically, U–Ni–AA is the most convenient catalyst for vapor-phase reduction. The reduction can even be carried out in the usual Sabatier apparatus for ordinary vapor-phase reduction.

3. 3. Details on Individual Urushibara Catalysts

(*a*) *U–Ni–A and U–Ni–B*

Of all the Urushibara catalysts, U–Ni–A and U–Ni–B are the most

commonly used and have the widest applications. Either catalyst will serve for the same catalytic reduction, as there is no substantial difference in activity between the two catalysts. It sometimes happens, however, that one of them is to be preferred according to the kind and purity of the substance to be reduced, or according to the reaction conditions.

Both U–Ni–A and U–Ni–B are produced from the same precipitated nickel that is deposited by the reaction between nickel salt solution and zinc dust. The precipitated nickel digested with acetic acid (or propionic acid) gives rise to U–Ni–A, and that digested with sodium hydroxide gives rise to U–Ni–B. In the latter case, the activity of the catalyst is somewhat reduced when the precipitated nickel is treated with an alkali solution of too high a concentration at too high a temperature, or when digestion is continued for a long time until the evolution of hydrogen subsides. Highly active U–Ni–B is obtained when the precipitated nickel is warmed with an approximately 10% solution of caustic alkali for 15 minutes. It contains considerable amounts of undissolved zinc and zinc oxide. In contrast, a good result is obtained in acetic acid treatment only when digestion is continued to such an extent that the zinc and zinc compounds almost completely dissolve away, and a small portion of nickel itself is dissolved to make the solution greenish. U–Ni–A consists of 70–80% nickel, together with a small amount of zinc folded into the former, and little, if any, zinc compounds are contained in it. The same amount of precipitated nickel prepared from nickel chloride and containing 1 g of nickel metal gives rise to Urushibara catalysts of different quantities; the gross weight of U–Ni–A is 1.1–1.4 g (nickel content ca. 0.85 g), whereas that of U–Ni–B amounts to as much as 5–10 g (nickel content nearly 1 g), the latter being far more bulky.

A neutral catalyst is readily obtained when U–Ni–A is washed a few times with water after preparation. In contrast, alkali combines with U–Ni–B so firmly that a trace amount of alkali can not be removed without much difficulty. When alkali treated precipitated nickel, which is washed twice with water and twice with ethanol, is used in catalytic reduction, the solution in which the reduction takes place becomes weakly alkaline (pH 9–10), as indicated by the pink color of phenolphthalein. Alkali-treated precipitated nickel, which is washed 5–6 times either with water or with ethanol, makes the solution only faintly alkaline, almost neutral to phenolphthalein (pH 8–9). Trace amounts of alkali are ultimately removed only when the catalyst is

washed with water ten times or more, and subsequently many times with ethanol (or other solvent to be used in the reduction process) to replace the wash-water.

U–Ni–B is effectively employed in catalytic reductions for which the presence of alkali is favorable; whereas U–Ni–A is appropriate for those reductions where the presence of alkali interferes. For example, a trace amount of alkali favors the reduction of ketones, aldehydes, nitriles, and oximes, for which the use of U–Ni–B is desirable. On the other hand, the reduction of aromatic nitro compounds is hindered by the presence of alkali and U–Ni–A can conveniently be used in this case.

It is nevertheless true that U–Ni–B can be used in neutral reductions, if it is washed thoroughly with water to completely remove alkali, and U–Ni–A can be used in the same reductions that are effectively conducted in the presence of U–Ni–B, provided a small amount of alkali is added. This is compatible with the fact that the activities of these two catalysts do not differ substantially from each other.

The above difference in the natures of U–Ni–A and U–Ni–B is successfully applied to selective reduction. For instance, *m*-nitroacetophenone gives *m*-aminoacetophenone in good yield in the presence of U–Ni–A or thoroughly washed U–Ni–B.[19]

U–Ni–A is far less bulky than U–Ni–B, and has the apparent advantage that it can be readily dispersed into solution when used in liquid-phase reduction. This matters little in a reduction under atmospheric pressure, as the reaction vessel can be shaken as vigorously as necessary to obtain thorough dispersion. In a high-pressure reduction, especially in a large scale reduction in a high capacity autoclave, however, the efficiency of reduction is mainly governed by the dispersability of fine catalyst particles into the solution. In such cases, U–Ni–B has a disadvantage, and in liquid-phase reduction at high pressure the use of U–Ni–A is always preferable. Addition of an appropriate amount of alkali may, however, be required in certain cases.

(*b*) *U–Ni–BA*

U–Ni–BA is prepared by the alkali treatment of the precipitated nickel which is obtained from nickel chloride solution and aluminum, instead of zinc dust. As the preparation of the precipitated nickel in this case requires much time, it is advisable to prepare and store in advance a large quantity of precipitated nickel, from which the required amount is occasionally removed and treated with alkali.

The U–Ni–BA catalyst consists primarily of nickel metal, along with

a small amount of contamiant, so that the bulk of the catalyst is greatly reduced, and is even smaller than that of U–Ni–A for the same nickel content.

The main characteristic of U–Ni–BA is its ability to hydrogenate aromatic rings of benzene and naphthalene and their derivatives. U–Ni–A and U–Ni–B can hydrogenate phenols to cyclohexanols, but are inactive to other aromatic compounds. On the contrary, U–Ni–BA is effective for almost every aromatic compound, including phenols.[31]

U–Ni–BA, like U–Ni–A and U–Ni–B, can be used for the hydrogenation of olefins, or the reduction of carbonyl and nitro compounds, but it gives somewhat poorer results. We can see this in the high-pressure reduction of acetophenone.[36] For general purposes other than for benzene ring hydrogenation, the use of U–Ni–A or U–Ni–B, with their high activity, stability, and availability is recommended.

(*c*) *U–Ni–AA*

U–Ni–AA is prepared by warming the precipitated nickel which is deposited from nickel chloride solution by aluminum grains, with acetic acid saturated with sodium chloride. It consists of aluminum grains coated by nickel, as the nickel metal deposited on aluminum grains does not separate from the latter, which remain undissolved after acetic acid treatment owing to the mild reaction between aluminum metal and acetic acid. As the aluminum grains which support the nickel metal act as a carrier, U–Ni–AA can most conveniently be used for a vapor-phase reduction.[26]

It is to be noted that the use of U–Ni–AA is not confined to vapor-phase reduction; it is also suitable for liquid-phase hydrogenation at room temperature and atmospheric pressure. This can be seen from the reduction of nitrobenzene in ethanol which, in the presence of U–Ni–AA, gives aniline in a 70% yield.

(*d*) *U–Ni–C Catalysts*

To promote the activity of U–Ni–A or U–Ni–B, it is desirable to reduce the particle size of the catalyst so as to facilitate its dispersion into solution. U–Ni–C catalysts comply with this requirement.

The particle size of Urushibara catalysts is seemingly determined by that of the precipitated nickel. To reduce the particle size of the precipitated nickel, it is necessary to retard the velocity of the ion-exchange reaction; that is, to retard the speed of deposition of nickel. The optimum conditions for the slow and uniform deposition of nickel

on zinc dust have been established. The precipitated nickel wihch is prepared by the reaction of zinc dust with nickel chloride solution of an appropriate concentration, either at room temperature or with cooling by running water or ice, is treated again in the cold with acetic acid or sodium hydroxide solution. In this way we obtain U–Ni–CA and U–Ni–CB. These catalysts, compared with ordinary Urushibara nickel catalysts, have a smaller particle size and exhibit higher activity, especially for liquid-phase reduction in an autoclave.[34] These catalysts, however, require much time for preparation, and therefore lack the distinguishing characteristic of the general Urushibara nickel catalysts—namely, speed in preparation.

(e) U–Ni(s) Catalysts

Another modified preparation of Urushibara nickel catalysts consists of the addition of nickel chloride crystals, instead of a nickel chloride solution, to zinc dust mixed with a small amount of water. Owing to the heat of reaction, local reaction is promoted and precipitated nickel is formed in a few minutes. It is digested with acid or alkali in the usual way, giving rise to two kinds of catalyst. They are U–Ni–A(s) and U–Ni–B(s).

The extreme ease with which the precipitated nickel is produced allows the U–Ni(s) catalysts to be prepared very quickly. This ease itself might mislead one to presume that the catalysts would have impaired activities. Nevertheless, they are sufficiently active for use in almost every reduction, and their activities are very close to, although not as high as, those of ordinary Urushibara nickel catalysts. For practical purposes, they may be widely used because of their simple preparation and high activities.

(f) U–Ni–A(HCl)

The use of hydrochloric acid in the digestion of the precipitated nickel greatly reduces catalytic activity. Therefore, U–Ni–A(HCl), which is obtained by treating the precipitated nickel with hydrochloric acid, is inadequate for ordinary purposes, except in certain instances where high activity is not desirable. Though the catalyst gives fairly good results in the partial hydrogenation of acetylenic compounds (see Section 6. 5. 4), it is practically of little use because the Urushibara iron catalyst is most profitable for such partial hydrogenations.

U–Ni–A(HCl) and U–Ni–A(s) (HCl) may be used for the reduction of benzoin under high pressure, but their activities can not compare with

those of other U–Ni–A catalysts.[37] The cause of the impaired activity is apparently that a considerable amount of nickel is dissolved when the precipitated nickel is treated with hydrochloric acid, so that the nickel content of the catalyst is diminished, or that some chlorine compound is adsorbed on the surface of the catalyst and behaves as a kind of poison.

(g) U–Ni–NH_3

Precipitated nickel also gives rise to an Urushibara nickel catalyst on treatment with aqueous ammonia instead of sodium hydroxide. This is U–Ni–NH_3. A considerable amount of ammonia remains even after washing with water. Ammonia is adsorbed on the catalyst far more strongly than is sodium hydroxide on U–Ni–B.

Catalytic reduction of nitriles or oximes yields primary amines together with secondary amines. The use of ammonia especially favors the formation of the former. Therefore, the yields of primary amines in the catalytic reduction of these compounds are higher in the presence of U–Ni–NH_3 than in the presence of U–Ni–B.[30]

(h) U–Co Catalysts

Urushibara cobalt catalysts are modifications of the Urushibara nickel catalysts, just as Raney cobalt is a congener of Raney nickel. Their activities compare with that of Raney cobalt and have properties very similar to the corresponding useful nickel catalysts. However, they are less useful for general purposes, as their activities are somewhat less and they are more expensive. In catalytic reduction of nitriles or oximes Raney cobalt surpasses Raney nickel in depressing the formation of accompanying undesirable secondary amines. Likewise, the U–Co–B catalyst was used for the same purpose and proved to be more effective than U–Ni–B.[30] In general, the cobalt catalysts are known to be less active than the nickel catalysts for hydrogenation of the ethylenic bond, U–Co–B can effect the selective reduction of unsaturated nitriles to unsaturated amines, leaving the ethylenic linkage intact.[8]

It should be remembered that U–Co–B is entirely inactive when used in ethanol saturated with ammonia. Therefore, ammonia should be precluded from U–Co–B, even in the reduction of nitriles for which the presence of ammonia is usually preferable.[8]

(i) U–Cu Catalysts

In general, copper catalysts have an outstanding disadvantage in

hydrogenation. This is the case with the Urushibara copper catalyst, which, like the Raney copper catalyst, is far less active than the corresponding nickel or cobalt catalysts. The Urushibara copper catalyst is quite unfit for catalytic reduction under atmospheric pressure, but can be used in reduction under higher pressure, provided the reaction is carried out at a temperature higher than would be appropriate for the nickel catalyst.

(*j*) *U–Fe Catalysts*

Crystals of iron(II) or iron(III) chloride are added to zinc dust mixed with a small amount of water, affording precipitated iron which, on treatment with acetic acid, furnishes U–Fe(II) or U–Fe(III), respectively. These Urushibara iron catalysts, like the Raney iron catalyst, have a distinct specificity in favoring the partial hydrogenation of acetylenic compounds to ethylenic compounds.[38] Either U–Fe(II) or U–Fe(III) is suitable for this purpose. It must be remembered, however, that U–Fe–BA, which is prepared from iron(III) chloride solution and aluminum grains, is completely inactive in the hydrogenation of acetylenic compounds.

4. Preparation of the Urushibara Catalysts

4.1. Urushibara Nickel Catalysts

Preparation of Urushibara catalysts is carried out in two stages. The first stage involves the deposition of nickel metal by reaction between a soluble nickel salt and a metal which is more electropositive than nickel. The second stage consists in the treatment of the precipitated nickel with alkali or acid to yield an active catalyst; treatment with a base gives rise to U–Ni–B, whereas treatment with an acid gives rise to U–Ni–A. It is established that the reaction conditions in the first stage, where the precipitated nickel is prepared, have a striking influence upon the activity of the catalyst which is produced.

Zinc, aluminum, and magnesium have been tested for use in precipitating nickel metal from its salt, but as zinc dust has the greatest advantage in the ease with which it is handled, it is being used exclusively in the preparation of ordinary Urushibara catalysts.

As for the soluble nickel salt, the chloride, nitrate, sulfate, and acetate were successively employed, and nickel chloride was found to be the most appropriate for obtaining a catalyst of high activity. Nickel nitrate solution hardly reacts with zinc dust, and nickel sulfate solution yields a catalyst of rather low activity. Nickel acetate, on the contrary, readily yields precipitated nickel, which proves to give as good a catalyst as that obtainable from nickel chloride.

Two methods are available in effecting the reaction between nickel chloride solution and zinc dust. One is the addition of zinc dust to the nickel chloride solution, and the other is the addition of nickel chloride solution to the zinc dust. In an early stage of investigation, the precipitated nickel was prepared exclusively by way of the first method, but it gradually turned out that when zinc dust was used in large excess relative to the amount of nickel chloride, the second method was preferable in that it gave a catalyst of striking activity. Later, a simplified procedure was devised in which nickel chloride crystals were added with stirring to the zinc dust mixed with a small amount of water, giving rise to an Urushibara nickel catalyst of comparatively high activity.

Sodium hydroxide is usually employed in the alkali treatment and activation of precipitated nickel. Potassium hydroxide gives a catalyst of as high an activity, although it requires a longer digestion time. Aqueous ammonia may be used instead of caustic alkali, but the resultant activity is somewhat lower.

Acetic acid is most commonly used as the digesting agent for U–Ni–A. Formic, propionic, and butyric acids were also examined; the details will be described later. In spite of the advantage of propionic over acetic acid in yielding a better catalyst, the latter has the most general application because of its practical convenience. Hydrochloric acid was also examined, but the activity brought about was quite small.

The activity of the Urushibara nickel catalyst gradually increased as successive examinations and improvements were applied to the preparative method. We shall first present the preparative method for U–Ni–B which was employed in an early period of this investigation.[7]

Preparation 1: U–Ni–B

Ten ml of solution prepared from 2 g of crystalline nickel chloride is warmed to 80–90°C and added, over a period of 1–2 minutes with stirring, to 5 g of zinc dust, which has been mixed with a small amount of water and placed in a water bath of the same temperature. Immediately afterward, the precipitate is filtered off with a sintered glass filter and washed with a small amount of hot distilled water. It is then plunged into 100 ml of 10 % sodium hydroxide solution as quickly as possible and left standing for 15–25 minutes on a water bath at 50–60°C with occasional stirring. The supernatant liquid is decanted, and the remainder is washed with two 40 ml portions of distilled water at 50–60°C. Then the wash-water is replaced by ethanol. The catalyst, containing 0.45 g of nickel adhering to 2 g of zinc, is thus obtained.

The last step, in which ethanol replaces the wash-water, can be omitted when reduction is to be carried out in an aqueous solution.

4. 1. 1. Optimum Conditions for the Preparation of Catalysts

(*a*) *Relative Amounts of Nickel and Zinc*

To establish the optimum conditions for obtaining a catalyst of high activity, the amount of zinc dust to be brought into reaction with a fixed amount of nickel chloride has been examined. Several batches of precipitated nickel were prepared from 4.04 g of $NiCl_2 \cdot 6H_2O$ and amounts of zinc dust varying from 5 to 10 g. They were digested with

Table 4–1. Variation of Catalytic Activity According to the Amount of Either Zinc Dust or Sodium Hydroxide Solution Used for the Preparation of U–Ni–B

Catalyst: U–Ni–B from $NiCl_2$ solution containing 1 g of Ni
Sample: 0.04 mole of cyclohexanone (3.92 g) in ethanol (25 ml)
Conditions: Atmospheric pressure, 25–28°C

Zn (g) \ 10% NaOH aq. (ml)	20	40	60	80	100	120	160
10	221	263		294		286	256
9			215	322	280		
8		226	279				
7	249	216					
5	182	172	144				

The values are the volumes (ml) of hydrogen absorbed during first 10 minutes.

10% sodium hydroxide solution, yielding different amounts of U–Ni–B, each of which contained 1 g of nickel metal. A comparison of the activities of these U–Ni–B catalysts, by utilizing them in the reduction of cyclohexanone, revealed that the addition of 9–10 g of zinc dust to 1 g of nickel gave the best result. This experiment was carried out together with that in the next paragraph, and the combined data are illustrated in Table 4–1.

(*b*) *Alkali Treatment of Precipitated Nickel*

The amount of 10 % sodium hydroxide solution to be used for activating the precipitated nickel has been examined. The experiment was carried out together with that described in the preceding paragraph and each batch of precipitated nickel described above was digested with varying amounts of 10 % sodium hydroxide solution to yield various U–Ni–B catalysts. An ion-exchange reaction between nickel chloride solution and zinc dust was carried out on a boiling water bath and alkali digestion was carried out at 50–60°C.

To compare the activities, a solution of 0.04 mole (3.92 g) of cyclohexanone in 25 ml of ethanol was reduced in the presence of each catalyst at 25–28°C, and the amount of hydrogen absorbed during the first ten minutes was determined. The results are summarized in Table 4–1. We see that 9–10 g of zinc dust to 1 g of nickel combined with 80 ml of 10 % sodium hydroxide solution for digestion gives the best U–Ni–B. This catalyst, however, contains large quantities of zinc,

zinc hydroxide, and zinc oxide, and the unwieldy bulk of the catalyst, weighing as much as 10 g, limits its application to reductions.

To obtain a catalyst of less bulk by reducing the amounts of zinc and zinc hydroxide in the catalyst, it is sufficient to raise the concentration of alkali or the temperature of digestion; however, this procedure causes an inevitable reduction in catalytic activity. A catalyst for practical use which is less bulky, though somewhat less active, than the best catalyst mentioned above is prepared by choosing the reaction conditions so as to make the gross weight of the catalyst amount to 6–7 g per gram of nickel. The present standard preparation of U–Ni–B involves 160 ml of 10 % sodium hydroxide solution for digesting the precipitated nickel which contains 1 g of nickel.

(*c*) *Washing U–Ni–B and Catalytic Activity*

U–Ni–B obtained by digesting the precipitated nickel with sodium hydroxide solution is used for reduction after being washed free from alkali with water. For substances such as ketones, nitriles, oximes, and phenols, which are rapidly reduced in the presence of alkali, U–Ni–B should be prepared without thorough washing, so that a finite amount of alkali remains in the catalyst. On the other hand, for reductions in which the presence of alkali interferes, we must wash the alkali-treated catalyst thoroughly with water.

Care should be taken to preserve catalytic activity during the washing. Washing in a stream of hydrogen, as in Adkins and Billica's method of preparing Raney nickel W–6,*1) which is probably the most advisable process, is, however, very troublesome for practical application. Information is available regarding the effect of the washing temperature on catalytic activity. It describes the change in activity for the reduction of nitrobenzene according to the temperature at which the catalyst is washed in air. The catalyst is washed with distilled water, which is boiled once and then brought to the temperature specified. The activity of the catalyst, which is realized after washing with 50 ml portions of water either ten times or until the wash-water is no longer alkaline to phenolphthalein, is illustrated in Fig. 4–1. Here the activity refers to the amount of hydrogen absorbed during the first 20 minutes, when 0.02 mole (2.46 g) of nitrobenzene in 20 ml of ethanol is reduced at 25°C under atmospheric pressure. We see that good activity is secured

*1) H. Adkins and H. R. Billica, *J. Amer. Chem. Soc.*, **70**, 695 (1948); Organic Syntheses, Vol. 29, p. 24 (1949); Coll. Vol. 3, p. 176 (1955).

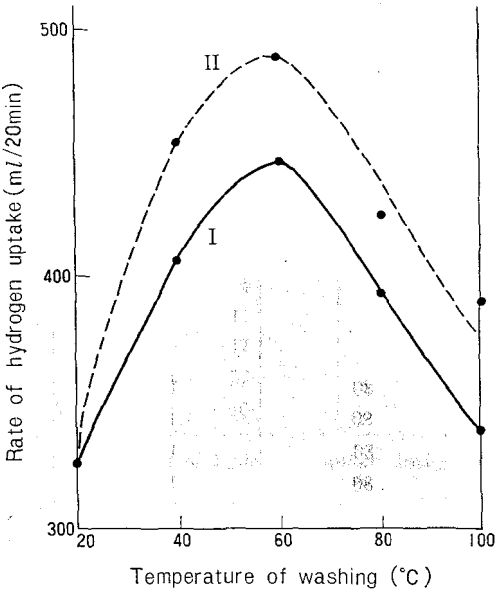


Fig. 4–1. Variation of Catalytic Activity According to the Temperature of Washing

Catalyst: U–Ni–B containing 0.5 g of Ni
Sample: 0.02 mole Nitrobenzene (2.4 g) in 20 ml ethanol
Conditions: Atmospheric Pressure, 25°C
The rates refer to the amounts of hydrogen uptake (ml) during the first 20 minutes.
I: Washing with ten 50 ml portions of purified water
II: Washing with the same aliquots of purified water, until the wash-water is neutral to phenolphthalein.

when distilled water at 50–60°C is used for washing, the temperature being the same as that of alkali digestion.

(*d*) *Treatment of Precipitated Nickel with Acids*

Information is also available regarding the change in catalytic activity with the amount or concentration of acetic acid used to digest the precipitated nickel. Several portions of the precipitated nickel, each of which was prepared by adding 5 g of zinc dust to a nickel chloride solution containing 0.5 g of nickel, were warmed with varying amounts of acetic acid. When the reaction had nearly subsided (3–5 minutes), the remaining solids were washed with distilled water at 50–60°C. A solu-

Table 4–2. Variation of Catalytic Activity According to the Amount of Acetic Acid Used for the Treatment of Precipitated Nickel.

Catalyst: U-Ni-A from $NiCl_2$ containing 0.5 g of Ni
Sample: 0.02 mole of nitrobenzene (2.46 g) in ethanol (20 ml)
Conditions: Atmospheric pressure, 25°C

Amount of acetic acid (ml)	Total volume of acid solution (ml)	Concentration of acid (%)	Activity[a] (ml)
0	80	0	9
4	80	5	61
6	80	7.5	78
8	98	8.2	135
8	80	10	176
10	80	12.5	256
11	80	13.8	263
12	80	15	243
12	100	12	246
12	120	10	213
14	80	17.5	209

[a] Activity refers to the amount of hydrogen uptake during first 10 minutes.

tion of 0.02 mole (2.46 g) of nitrobenzene in 20 ml of ethanol was reduced at 25°C under atmospheric pressure in the presence of each catalyst, and the amount of hydrogen absorbed during the first 10 minutes was recorded. The results are shown in Table 4–2.

It turns out that an insufficient amount of acetic acid causes a reduction in catalytic activity, whereas enough acid, sufficient not only for the complete dissolution of zinc metal but also for the partial dissolution of the nickel itself, gives rise to a catalyst of high activity. The highest activity is obtained when 80 ml of ca. 13 % solution is used for digestion.

Pertinent data for catalysts prepared by digesting the precipitated nickel with formic acid, propionic acid, butyric acid, and hydrochloric acid is listed in Table 4–3.

We see that high activity is obtained when acetic or propionic acid is used to digest the precipitated nickel, the latter giving the best catalyst. Formic and butyric acids do not activate the catalyst to any great extent. A strong acid, such as hydrochloric acid, greatly reduces activity which, however, can be recovered to a considerable extent when the catalyst is treated subsequently with caustic alkali. It is supposed that hydro-

Table 4–3. Variation of Catalytic Activity According to the Kind of Digesting Agent

Catalyst: U–Ni–A from $NiCl_2$ containing 0.5 g of Ni
Sample: 0.02 mole of nitrobenzene (2.46 g) in ethanol (20 ml)
Conditions: Atmospheric pressure, 25°C

Acid	Amount of acid required for maximum activity (ml)	Total volume of acid solution (ml)	Activity[a] (ml)
formic acid (80%)	8	80	72
acetic acid	11	80	263
propionic acid	17	80	303
butyric acid	30	80	76
hydrochloric acid (37%)	10	80	5

[a] Activity refers to the amount of hydrogen uptake during first 10 minutes.

chloric acid treatment causes deposition of an unidentified poisonous chemical species containing chlorine and that the catalytic activity is recovered when this is removed by alkali treatment.

U–Ni–A catalyst prepared by way of acetic acid or propionic acid retains as good as activity as an alkali-treated N–Ni–B would show. For example, 265 ml of hydrogen is absorbed during the first ten minutes when nitrobenzene is reduced in the presence of the best U–Ni–B catalyst under the conditions indicated in Table 4–3, the value being in good accord with that obtained for U–Ni–A.

(*e*) *Conditions for the Preparation of Precipitated Nickel*

As we shall see later, an intimate relation exists between the catalytic activity and the crystal structure of the catalyst metal. It is generally believed that the crystal structure of an Urushibara nickel catalyst is determined at the stage where nickel is deposited on the surface of the zinc metal. Hence the activity of a catalyst will depend largely on the conditions under which the precipitated metal is produced. This relation was noticed in an early period of the investigation of Urushibara nickel catalysts, and was established by later work, in which the activities of different U–Ni–A catalysts, prepared from different precipitated nickels, were compared with each other under the same conditions. The results are illustrated in Table 4–4, for which a number of precipitated nickels were produced by varying the concentration of the original nickel chloride solution, or by varying the temperature at which the ion-

Table 4–4. Activities of U–Ni–A Catalysts Prepared from Nickel Precipitated under Various Conditions

Material: Nickel precipitated under various conditions from 5 g of zinc dust and $NiCl_2$ solution containing 0.5 g of Ni
Treatment: 80 ml of 13% acetic acid
Sample: Nitrobenzene (0.82 g) in ethanol (20 ml)
Conditions: Atmospheric pressure, 25°C

Concentration of nickel chloride solution	Temperature of reaction with zinc dust (°C)	Hydrogen uptake (ml/min)
0.5 g Ni in 50 ml	room temp. to 100	19
0.5 g Ni in 5 ml	room temp.	25
0.5 g Ni in 50 ml	100	25
0.5 g Ni in 5 ml	100	29

exchange reaction took place. The values, which refer to activities, are the amounts of hydrogen absorbed during the first 5 minutes of the reduction of nitrobenzene in the presence of these catalysts under atmospheric pressure. They are averaged over a number of runs.

We can see that the more vigorous the reaction between nickel chloride solution and zinc dust, the more active the catalyst produced.

The recommended procedure is as follows: Nickel chloride solution of maximally high concentration is added with strong stirring to an excess amount of zinc dust mixed with a small amount of water. The resultant mixture is then placed on a boiling water bath. A high reaction temperature and a short preparation time favor high activity.

4. 1. 2. Standard Method of Preparation of U–Ni–B and U–Ni–A

The preceding discussion has led to a standardized method for the preparation of U–Ni–B and U–Ni–A.[4),5)] Catalysts so prepared exhibit the highest activities and are the most profitable for practical use. The procedure for the preparation of the precipitated nickel is the same for both catalysts; they are different because of their activation processes. We shall present in the following a standard method for preparing Urushibara nickel catalysts, each containing 1 g of nickel.

Preparation 2: The Precipitated Nickel

Place 10 g of zinc dust (Note 1) in a 100 ml round-bottomed flask (Note 2) and add 3 ml of distilled water. A good stirrer, extending almost to the bottom, is fitted and the flask is heated on a boiling water-

bath. Dissolve nickel chloride crystals in distilled water in such a way that a 10 ml solution containing 1 g of nickel is obtained (Note 3). Heat to boiling in a beaker and pour within a few seconds (Note 4) into the flask containing the slurry of zinc dust and water with vigorous stirring. As a vigorous reaction takes place, the contents should be carefully watched for flooding. The vigorous reaction will soon subside. Stop stirring and filter with suction the solid contents of the flask with a sintered glass filter and wash with about 200 ml of hot water (Note 5). Place the solid mass with a stainless steel spatula into a 300 ml beaker or Erlenmeyer flask for digestion. Washing on the sintered glass filter may be replaced by decantation with several portions of hot water in a beaker.

Notes: 1) The zinc dust should be as fine as possible; its purity, however, need not be of the highest grade. Commercially available zinc dust is sufficient. The presence of zinc oxide is permissible. Zinc dust containing 10 % or more of zinc oxide has been used with success. However, as catalysts obtained from zinc dusts of different grades may have different activities, zinc dust from the same package should be used in order to obtain catalysts of like activity, as are required in comparative studies.

2) If too small a flask is used, the contents may run over when a vigorous ion-exchange reaction takes place. An ordinary round-bottomed flask may be used; a wide-necked " egg-shaped " flask is more appropriate in that the contents can be removed more easily. A three-necked flask is also convenient, especially for comparatively large scale preparation of precipitated nickel.

3) Nickel chloride may be commercially available material of a chemically pure grade. One gram of nickel corresponds to 4.04 g of the nickel chloride crystals $NiCl_2 \cdot 6H_2O$; however, as the crystals are hygroscopic, direct weighing is meaningless. To obtain precipitated nickel of known nickel content, as is required in a comparative study of catalysts prepared under various conditions, it is recommended that the solution be prepared in large quantities by direct weighing so that about 1 g of nickel is contained in 10 ml of solution, the exact concentration of which is then determined with dimethylglyoxime. In this method, the appropriate amount of solution is pipetted prior to use. For ordinary reductions, however, an exact determination of the nickel content is not necessary, and a catalyst containing roughly 1 g of nickel is obtained from 4 g of nickel chloride crystals dissolved in 10 ml of water.

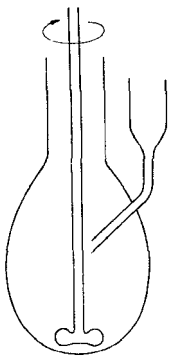


Fig. 4–2. Flask for the Preparation of the Precipitated Nickel

4) An ordinary pipet is not convenient for adding the nickel chloride solution to the zinc dust, as discharge is time consuming, which inevitably causes a reduction in catalytic activity. A pipet of which the tip has been cut off allows the solution to run out quickly and uniformly. The apparatus shown in Fig. 4–2, equipped with an inlet tube through which the nickel chloride solution can be poured from a beaker, allows the uniform addition of solution in 2 to 3 seconds.
5) The product is a dark gray powder-like mass. The wet precipitated nickel, as it stands, is usually subjected to the subsequent digestion process. It has been found, however, that the precipitated nickel always gives an active catalyst on treatment with alkalis or acids, even if it is dried previously at about 100°C and stored in air.[36] Therefore, a large amount of precipitated nickel may be prepared and stored dry; the requisite amount is then occasionally taken out to produce a catalyst, of which the activity is by no means unsatisfactory for practical purposes.

Preparation 3: U–Ni–B

To a 300 ml beaker or Erlenmeyer flask containing 160 ml of 10% sodium hydroxide solution (Note 6) is added (Note 7) the precipitated nickel (Preparation 2). It is recommended that a part of the sodium hydroxide solution be reserved for washing out the precipitated nickel on a sintered glass filter. As the precipitated nickel reacts with the sodium hydroxide solution with the violent evolution of hydrogen, care should be taken that the contents do not run over. The reaction vessel is heated on a water bath at 50–55°C with gentle stirring for 15–

20 minutes (Note 8). The supernatant liquid is decanted, and the remainder washed with two or three 40 ml portions of distilled water, which have been boiled in advance and cooled to 50–60°C. Each time the wash-water is decanted (Note 9), and the remainder is washed with the solvent, e.g., ethanol, to be used in the subsequent reduction, and is then transferred together with the solvent to the reduction vessel. The solid should always be covered with water or solvent after the alkali treatment, so that it is protected from contact with the air.

The product is U–Ni–B, a dark gray powder-like solid. U–Ni–B, prepared from nickel chloride containing 1 g of nickel, consists of about 0.95 g of nickel and 4–5 g of zinc, together with small amounts of zinc oxide and zinc hydroxide, the total weight amounting to 5–7 g.

Notes: 6) 80 ml of 10 % sodium hydroxide solution instead of 160 ml yields a more active catalyst; however, it is more bulky and the gross weight amounts to as much as 10 g, because the zinc is dissolved to a lesser extent.

7) The procedure was designed so as to avoid contact with air. However, as it has been verified that drying of the precipitated nickel has little effect upon catalytic activity, one may take an alternative procedure, in which the precipitated nickel is first placed in a beaker, and sodium hydroxide solution is added to it with stirring. The latter process is preferred because liquid overflow due to the vigorous reaction can easily be controlled.

8) The activity of the catalyst is reduced when the temperature at which the precipitated nickel is warmed with sodium hydroxide solution is too high, or when digestion continues so long that the evolution of hydrogen gas subsides.

9) A trace of alkali remains in the catalyst, as revealed by the pink color of phenolphthalein, if rinsing is carried out only 2 or 3 times. In cases where the presence of alkali is undesirable, according to the kind of material to be reduced, washing should be repeated many times until the wash-water is no longer alkaline to phenolphthalein. In such cases, adsorbed alkali can be removed with considerable ease if the catalyst is first washed with two or three portions of warm water, then with saturated sodium chloride solution, and finally several times again with warm water.

Preparation 4: U–Ni–A

To a 300 ml beaker or Erlenmeyer flask containing 160 ml of 13%

acetic acid (Note 10) is added (Note 11) the precipitated nickel (Preparation 2). It is recommended that a part of the aqueous acetic acid be reserved for washing out the precipitated nickel on a sintered glass filter. As the addition of precipitated nickel to acetic acid results in the violent evolution of hydrogen, the contents should be carefully watched to prevent running over. After stirring for 4–6 minutes at room temperature (Note 12), the evolution of hydrogen gas gradually subsides and most of the zinc and zinc compounds dissolve away, a black powderlike solid having adsorbed hydrogen appearing on the surface of the solution. When the solution becomes greenish (Note 13), it is carefully filtered and the black solid is collected on a sintered glass filter. It is washed with 200 ml of distilled water (Note 14), which has been boiled in advance and cooled to 50–60°C, then with the solvent to be used in the subsequent reduction (ethanol, for example), to replace the wash-water. The whole of the catalyst is put into the reduction vessel together with the solvent (Note 15). The catalyst on the sintered glass filter should be protected from contact with air, and washing repeated in such a way that the wash-liquid on the catalyst is not exhausted.

The U–Ni–A obtained is a black powder-like solid. U–Ni–A from nickel chloride containing 1 g of nickel contains 0.8–0.85 g of nickel, together with a small amount of contaminants, such as zinc, and weighs 1.3–1.4 g.

Notes: 10) A catalyst of somewhat higher activity is obtained when 160 ml of 20 % propionic acid is used instead of acetic acid, and digestion is continued for 4–5 minutes at 50°C.

11) An alternative procedure may be employed, in which the precipitated nickel is first put into the beaker and then aqueous acetic acid is added with stirring (see Note 7).

12) Digestion may be carried out at 40°C on a water bath for 4 minutes.

13) Part of the nickel dissolves in acetic acid and produces a green color. When the solution is colorless, stirring should be continued until the color develops. In order to obtain a catalyst of high activity, it is necessary to allow digestion to proceed until green coloring develops. However, the catalyst should be filtered off as soon as the coloring appears, because a longer digestion diminishes the nickel content.

14) Acetic acid adsorbed on U–Ni–A can be removed by washing far more easily than can alkali.

15) An alternative method may be used as well, in which the catalyst is transferred to the reaction vessel by means of a small amount of

distilled water after washing is completed, and the wash-water is replaced with solvent by decantation.

4. 1. 3. U–Ni Catalysts Prepared from Nickel Acetate

Nickel acetate, in place of nickel chloride, gives an Urushibara nickel catalyst of like activity. As the reaction between nickel acetate and zinc dust is more violent than that between nickel chloride and zinc dust and is accompanied by strong bubbling of the reaction mixture, it must be carried out in a larger vessel with strong stirring.

Regarding the reduction of benzophenone, it has been established that U–Ni–B prepared from nickel acetate is somewhat more active than that from nickel chloride, whereas the reverse is true with U–Ni–A.[34]

Preparation 5: U–Ni–B from Nickel Acetate

On a boiling water bath, 4.24 g of nickel acetate, $Ni(CH_3CO_2)_2 \cdot 4H_2O$, is dissolved in 20 ml of water. The hot solution is added all at once with stirring to a hot mixture of 10 g of zinc dust and 10 ml of water, which is placed in a 500 ml beaker and warmed on another boiling water bath. As a vigorous reaction takes place and the reaction mixture begins to inflate, strong agitation is required to prevent the contents from running over. When the reaction subsides, 200 g of 10% sodium hydroxide solution is cautiously added to the reaction product with stirring. The temperature of the mixture is kept at 50–55°C for 15 minutes with occasional stirring. When the solid matter settles, the supernatant liquor is decanted and the solid is washed with two 100 ml portions of hot water, then with two 50 ml portions of the solvent to be used in the reduction, e.g., ethanol. In this way a bulky catalyst, weighing as much as 8.5–10.5 g, is obtained. The catalyst contains about 1 g of nickel, together with considerable amounts of zinc and zinc oxide and a very small amount of alkali.

Preparation 6: U–Ni–A from Nickel Acetate

To prepare U–Ni–A from nickel acetate, Preparation 5 should be modified as follows: To the precipitated nickel prepared in Preparation 5 is added, with stirring, 160 ml of 13 % acetic acid instead of caustic alkali. The mixture is left standing with occasional stirring until the evolution of hydrogen ceases and a solid rises to the surface of the greenish solution. The solid is collected on a sintered glass filter and washed with 200 ml of hot water, then with 100 ml of ethanol. The catalyst contains only small quantities of zinc and zinc oxide and weighs about 0.7 g.

4. 1. 4. U–Ni–C Catalyst

To obtain a precipitated metal of small particle size, it is necessary to retard the rate of the ion-exchange reaction. The rate of the ion-exchange reaction depends on several factors, such as the difference in the standard electrode potentials of zinc and the catalyst metal, the fineness of the zinc dust, the concentration of the solution of metal chloride, the temperature at which the precipitated metal is prepared, and the efficiency of agitation. Of these, only the temperature can be freely controlled; the other factors are mainly decided by the nature or quality of the chemicals. At low temperatures, the ion-exchange reaction takes place slowly and the metal separates out uniformly on the surface of the zinc dust, giving thereby a catalyst of small particle size (see the microphotographs shown in Fig. 5–2, Chapter 5). The precipitated nickel prepared at low temperatures gives a highly active Urushibara nickel catalyst.[34] Its preparation, however, requires so much time that speed of preparation, the unique characteristic of the Urushibara catalysts, is lost.

Preparation 7: U–Ni–CB

To a 100 ml flask containing 10 g of zinc dust and 4 ml of water is added 10 ml of an aqueous solution containing 4.04 g of nickel chloride, $NiCl_2 \cdot 6H_2O$. The mixture is stirred at room temperature, or while being cooled with water or ice, until the green color of the nickel ion disappears. The stirring may be interrupted after the first hour, as the ion-exchange reaction is practically complete after this period. The mixture should be left standing thereafter until the remaining faint color disappears. The whole process requires 3–4 hours. To prepare precipitated nickel on a large scale, it is advisable to cool the mixture with ice during the ion-exchange process. The slushy precipitate is transferred to a 300 ml beaker and washed with 200 ml of cold water. To digest the precipitated nickel, 160 g of cold 10 % sodium hydroxide solution is added to the beaker and the mixture is stirred for an hour. Cooling with water or ice is often required. When most of the solid settles, the upper liquor is carefully decanted and the solid is washed with two 100 ml portions of cold water and then with two 50 ml portions of solvent. The catalyst contains about 1 g of nickel; zinc, zinc oxide, and a trace amount of alkali are always present in the catalyst. Weight 8–11 g.

Preparation 8: U–Ni–CA

The precipitated nickel (Preparation 7) is transferred to a 500 ml beaker and is carefully treated with 200 ml of 10 % acetic acid while being cooled with water. After about 5 minutes, the liberation of hydrogen subsides and a solid comes to the surface of the green solution. The solid is collected on a sintered glass filter and washed with 200 ml of cold water, and then with 100 ml of solvent. The catalyst is a fine powder and weighs 0.6 to 0.8 g. It contains 0.4–0.5 g of nickel together with small amounts of zinc and zinc oxide.

4. 1. 5. Simplified Methods for the Preparation of Urushibara Nickel Catalysts

The reaction between nickel chloride solution and zinc dust is exothermic. Attempts were made to make use of the heat of reaction in accelerating the reaction and in simplifying the procedure. Attempts in which a concentrated nickel chloride solution was added to dry zinc dust failed, as the reaction took place too vigorously to permit thorough agitation, so that a uniform deposit of nickel metal onto the zinc could not be obtained. After a number of trials, it was found that the practicable method consisted of adding crystals of nickel chloride to zinc dust mixed with a small amount of water. By this method, good precipitated nickel is obtained in a few minutes.

Urushibara nickel catalysts prepared from this precipitated nickel are distinguished from ordinary catalysts by adding the bracketed letter (s) after the name, as in U–Ni–B(s) or U–Ni–A(s). In spite of their simple preparative method, the activities of the catalysts are by no means poor, and the hydrogenation of ketones has assured that they are sufficient for practical use.[37]

Preparation 9: Precipitated Nickel (Simplified Method)

4.04 g of commercial nickel chloride crystals ($NiCl_2 \cdot 6H_2O$) is added all at once to a 50 ml beaker containing 10 g of zinc dust which is mixed well with 4 ml of water, and the mixture is stirred with a glass rod. Reaction takes place and abruptly becomes violent. The reaction goes on for a few minutes and the mixture inflates into a slushy mass (Note 1). It is then washed with 200 ml of cold water, and the wash-water is removed by filtration or decantation. The precipitated nickel weighs about 13.5 g and contains about 1 g of nickel, together with zinc, zinc oxide, and zinc hydroxide chloride.

Notes: (1) The reaction begins at room temperature. As a vigorous reaction takes place, the temperature of the reaction mixture rises to 60–70° C owing to the heat of reaction. In large scale production, the temperature may rise to as high as 100° C, and often most of the water evaporates.

Preparation 10: U–Ni–B(s)

To precipitated nickel (Preparation 9) placed in a 300 ml beaker is added 160 g of 10 % sodium hydroxide solution with stirring. The resultant mixture is heated to 50° C on a water bath and stirred gently for 15 minutes. The supernatant liquor is decanted and the residue is washed with two 100 ml portions of water, then with the same amounts of solvent. Each time the wash-liquid is removed by decantation. The catalyst is a black powder and is less bulky than ordinary U–Ni–B (the latter is a grayish powder).

Preparation 11: U–Ni–A(s)

To precipitated nickel (Preparation 9) placed in a 300 ml beaker is added 150 ml of 20 % acetic acid and the mixture is stirred at room temperature. In a few minutes the evolution of hydrogen subsides and a black solid comes to the surface, when a green color should develop in the solution. At this time, the solid is collected on a sintered glass filter and washed with 200 ml of distilled water at 50–60° C. Before the wash-water is completely drained off, the solid is transferred to a 100 ml beaker with 50 ml of ethanol and the wash-liquid is decanted. The catalyst is further washed with two 50 ml portions of ethanol, and each time the supernatant liquor is decanted. The catalyst should be protected from air as carefully as possible after digestion.

4. 1. 6. Urushibara Nickel Catalyst Prepared with Aqueous Ammonia

Precipitated nickel treated with aqueous ammonia in place of sodium hydroxide gives U–Ni–NH_3.[30] A fairly large amount of ammonia remains in the catalyst even after washing with water.

Preparation 12: U–Ni–NH_3

Precipitated nickel containing about 1 g of nickel (Preparation 2) is added to 100 ml of 14 % aqueous ammonia (Note 1), and the mixture is stirred gently on a water bath at 50–60° C. After 15–20 minutes of digestion, the evolution of hydrogen gradually subsides. The mixture is left standing for a while and the supernatant liquor is decanted.

The solid is washed with two 20 ml portions of methanol or ethanol. In each case the mixture should be stirred well before the wash-liquid is decanted. The U–Ni–NH_3 obtained in this way is a grayish black powder (darker than U–Ni–B) and weighs about 8.6 g. It contains large amounts of zinc and zinc compounds.

Notes: (1) In contrast to the case of U–Ni–B, a large amount of aqueous ammonia, sufficient to dissolve away most of the zinc, does not paralyze the catalytic activity.

4. 1. 7. Urushibara Catalyst Prepared with Hydrochloric Acid

It is to be understood that digestion is the process where the precipitated nickel is activated by alkali or acid. It involves the removal of deactivating substances and the erosion of the nickel surfaces.[36] We have seen in a preceding chapter that acetic and propionic acids are good digesting agents, whereas formic, butyric, and hydrochloric acids give poorer results. The reduction of ketones has revealed that U–Ni–A(HCl) is much less active than any other U–Ni–A. Either a considerable amount of nickel may be lost from the catalyst during strong acid treatment, or some chlorine compound may be adsorbed on the surface of the catalyst to behave as a kind of poison.

Preparation 13: U–Ni–A(HCl)[37]

0.75 N Hydrochloric acid (480 ml) is added to precipitated nickel containing about 1 g of nickel (Preparation 2 or Preparation 9, simplified method) and the mixture is stirred at room temperature. Violent evolution of hydrogen takes place. After approximately one minute of agitation the solution becomes greenish, and a black solid comes to the surface of the solution. At this time, the solid is collected on a sintered glass filter and washed with 400 ml of distilled water. Particular care should be taken to prevent the solid from coming into contact with air. Before the wash-water is drained off completely, the catalyst is transferred into a 100 ml beaker with 50 ml of ethanol, and washed further with two 50 ml portions of ethanol. Each time the supernatant liquor is decanted.

4. 1. 8. U–Ni–BA

Aluminum can be used in place of zinc dust for precipitating nickel metal from its salt solution. In this case, nickel chloride is almost exclusively employed as the starting material. The catalyst U–Ni–BA,

obtained by treating the precipitated nickel with sodium hydroxide solution, shows a specific activity for aromatic ring hydrogenation.

(*a*) *Preparation of U–Ni–BA with Aluminum Powder*

Commercially available aluminum powder reacts with nickel chloride solution. However, the reaction is extremely vigorous and the solution foams up, carrying aluminum powder onto its surface together with the froth, which often flows out of the vessel. Practically, the reaction can not be controlled and treatment becomes extremely troublesome. A small amount of a surface-active agent may be added to suppress frothing, but this inevitably brings about a considerable reduction in activity. Therefore, U–Ni–BA obtained in this way is not a good catalyst, though it is still applicable to vapor-phase hydrogenation.[26]

Preparation 14: U–Ni–BA (for Vapor-phase Hydrogenation)

Ten grams of aluminum powder (200 mesh) are suspended in a small amount of water and the mixture is heated on a boiling water bath. Ten ml of nickel chloride solution at 90° C containing 4 g of $NiCl_2 \cdot 6H_2O$ crystals is then added to the hot suspension. When the vigorous exchange reaction subsides, the contents are heated to dryness and 200 ml of 20 % sodium hydroxide solution is added gradually. The contents should be stirred well and cooled with running water, as a vigorous exothermic reaction takes place while the aluminum is dissolved in a short time. The mixture is further heated for 5 minutes. The supernatant liquid is decanted and the residue is washed several times with water at 50–60° C, until the washing water is no longer alkaline to litmus. It is then washed thoroughly with methanol. The catalyst contains about 1 g of nickel.

(*b*) *Preparation of U–Ni–BA with Aluminum Grains*

Aluminum grains are best employed for preparing precipitated nickel from nickel chloride. As commercial aluminum grains are not uniform, they must be sifted to obtain grains of proper size. Grains of 40 to 80 mesh can best be used; a large mesh often makes the ion-exchange reaction difficult to control, giving a catalyst of non-uniform activity. As the commercial product is often stained, it must be treated with about 3 % sodium hydroxide solution to clean the surface before being used in preparing precipitated nickel.

Chips of aluminum wire of proper diameter are also useful, but the

chip size should be as small as possible in order to obtain good results.

Aluminum grains or chips undergo a violent exothermic reaction with nickel chloride solution, giving precipitated nickel. U–Ni–BA is obtained from this precipitated nickel *via* a method similar to that established for U–Ni–B.

Catalysts prepared under varying conditions have been compared with each other by applying them to the reduction of acetone, and a standard procedure for the preparation of U–Ni–BA catalyst, as shown below, has been established.[20] The usual U–Ni–B and U–Ni–A can be prepared in a short time, but the preparation of U–Ni–BA requires somewhat longer. This matters little, however, because it turns out that the nickel precipitated from nickel chloride and aluminum grains can be dried and stored; from this precipitated nickel a requisite amount may occasionally be taken out and digested with alkali, giving U–Ni–BA of reserved activity.[31]

Preparation 15: U–Ni–BA

Ten g of aluminum grains (ca. 100 mesh) are washed well with water and 50 ml of 3 % sodium hydroxide solution is added. A vigorous reaction takes place, with the liberation of hydrogen, and the solution becomes frothy with the elevation of temperature. Care should be taken to prevent overflow of the contents. When the clean surface of the grains appears, cold water is added to suppress frothing. The supernatant liquor is decanted and the residue is washed several times with water, until the wash-water is no longer alkaline to phenolphthalein.

The purified aluminum grains are transferred with 5–6 ml of water to a 500 ml wide-necked round-bottomed flask (Note 1) and heated on a boiling water bath. In another vessel 8.08 g of nickel chloride crystals, $NiCl_2 \cdot 6H_2O$, (corresponding to 2 g of nickel) is dissolved in water to a total volume of 20 ml. This solution is heated to boiling and is poured all at once on the aluminum grains. A violent reaction takes place and the solution froths, with fuming. It is left standing and stirred occasionally until nickel metal deposits on the surface of the aluminum grains, which become black and come up in part to the surface of the solution. The reaction mixture becomes slimy, and then slushy, and the green color disappears. Water evaporates on account of the heat of reaction until the whole mixture forms a viscous semi-solid, which, on cooling becomes nearly solid. The solid is crushed with a glass rod or stainless steel spatula, and washed two or three times with water to remove water-soluble products.

A small amount of water is added to the precipitated nickel, and it is cooled on an ice bath. To the well-cooled mixture, 250 g of 20 % sodium hydroxide solution is added in small portions with rapid stirring. Particular care should be taken to prevent the contents from overflowing, by cooling the mixture thoroughly with ice and by adding the alkali as slowly as possible while stirring well. The initial addition of even a small amount of alkali very often causes a violent reaction with a sudden evolution of hydrogen. Therefore, the portions of alkali to be added should be as small as possible, and later additions should be made at proper time intervals. The speed of addition should be controlled to maintain the temperature below 60° C. About 10 minutes are required for the addition of half the total amount of alkali. As the reaction gradually subsides, the other half may be added at once, whereupon the mixture should be stirred until the evolution of hydrogen ceases; warm to 50° C if necessary. The solution looks black on account of the suspension of fine black particles. Stirring is interrupted at this stage and the mixture is left standing for a few minutes. When the solid has almost settled, the supernatant liquor is decanted (Note 2) and the solid is washed with five 100 ml portions of water at 50–60° C, then with three 50 ml portions of ethanol. It is then transferred to the reduction vessel with the aid of the solvent. The catalyst is carefully protected from contact with air after alkali treatment.

Washing should be carried out with distilled water, which is removed each time by decantation.

The product, U–Ni–BA, contains about 2 g of nickel and a small amount of aluminum, together with a trace of alkali. It is a black powder-like solid, and its appearance resembles that of U–Ni–A. It contains very fine particles.

Notes: 1) A 500 ml beaker may also be used.
2) Usually fine particles will not settle down completely. As long contact with alkali reduces catalytic activity, the supernatant liquor should properly be removed just before it becomes clear.

Preparation 16: U–Ni–BA (from Stored Precipitated Nickel)

The precipitated nickel prepared according to Preparation 15 (Note 3) from 50 g of aluminum grains (100 mesh) and 100 ml of solution containing 40 g of $NiCl_2 \cdot 6H_2O$ (corresponding to ca. 10 g of nickel) is washed well with water. The slushy solid is collected on a Buchner funnel and dried and stored (Note 4). Its gross weight amounts to

about 70 g, but changes more or less according to experimental conditions.

To obtain U–Ni–BA containing about 2 g of nickel, one-fifth (about 14 g) of the dry precipitate is digested, following Preparation 15, with 250 g of 20% sodium hydroxide solution.

Notes: 3) A one liter vessel may be used.
4) The precipitated nickel may be dried in air. Drying under reduced pressure is desirable, but not necessary.

(*c*) *Modified Preparation of U–Ni–BA*

In Preparation 15, we have seen that the ion-exchange reaction is too violent to be controlled by external cooling, so that it fails to give U–Ni–BA catalysts of uniform activity even when the fixed procedure for the preparation is carefully followed. For this reason, the procedure may be modified as shown in Preparation 17.[32)]

Pre-treatment of aluminum grains by alkali has proved not to affect catalytic activity. It, however, requires thorough washing before use, to such an extent that the wash-water is completely neutral. The process requires a rather long time, but this can be reduced by employing dilute hydrochloric acid instead of alkali.

The activity of the U–Ni–BA catalyst, just as those of U–Ni–B and U–Ni–A, is mainly determined by the reaction conditions under which the precipitated nickel is produced, and is influenced little by the digestion process.

Experiments were carried out regarding the variation in catalytic activities according to the change in concentration of nickel chloride solution or according to the change in temperature during the ion-exchange reaction. When a solution of 4.04 g of nickel chloride crystals in 10 ml of water is heated to boiling, and is added to aluminum grains in a reaction vessel on a boiling water bath, the reaction is too vigorous from the beginning to be controlled by external cooling with water. This is still the case when the nickel chloride solution is diluted to half of its original concentration. Cooling is only attained by pouring water into the reacting solution. It has been established that when more dilute nickel chloride solution is heated to about 65° C (not to boiling), and added to aluminum grains at room temperature, one can control the reaction temperature at 70–80° C, which is appropriate for obtaining a catalyst of high activity. These results are summarized in Table 4–5.

Table 4–5. Effect of the Temperature of the $NiCl_2$–Al Ion-exchange Reaction on Catalytic Activity

Concentration of $NiCl_2$ solution (g-Ni/10 ml solution)	Temperature of $NiCl_2$ solution (°C)	Temperature of exchange reaction (°C)	Control of reaction temperature	Color of precipitated nickel	Activity of catalyst obtained
1	100	>90	impossible	gray	very weak
0.5	100	>90	difficult	gray	very weak
1	100	>90	possible by addition of water into the solution	dark gray	moderate
0.5	65	70~80	easy	black	strong

As a practical procedure, it is better to add comparatively dilute nickel chloride solution to aluminum grains at room temperature, then warm slightly on a water bath to start the reaction.

A mild exchange reaction gives a black nickel precipitate, and a more violent reaction tends to give a gray to dark gray nickel precipitate, which often exhibits a metallic luster. The color of the precipitated nickel clearly demonstrates that a violent reaction promotes crystallization of the nickel, which tends to decrease the catalytic activity.

In line with the above, a modified method of preparing U–Ni–BA was established. The catalyst was tried in the high pressure reduction of ethyl salicylate and proved to have a uniform activity. This modified procedure, though free from the drawback of non-uniform activity, requires a somewhat longer time for preparation.

Preparation 17: U–Ni–BA (Modified Method)

Place 50 g of aluminum grains (40–80 mesh) in a beaker, wash well with water, and add 50 ml of 6 N hydrochloric acid on a water bath. When the surface of the grains has become clean, the upper liquid is decanted and the aluminum is washed several times with water. It is then transferred to a 1 l wide-necked round-bottomed flask (Note 1), and 200 ml of solution containing 40.4 g of $NiCl_2 \cdot 6H_2O$ (corresponding to 10 g of nickel) is poured onto the aluminum grains all at once. The mixture is gently heated for a short time on a water bath to start a mild reaction. The temperature should be maintained below 70° C (Note 2) to prevent the reaction from getting out of control, and the mixture is stirred occasionally with a stainless steel spatula. The aluminum

grains gradually turn black as nickel deposits on them, and the reaction mixture becomes a viscous slush. When the reaction subsides, the mixture is heated on a boiling water bath (Note 3). A violent reaction begins again and the whole mixture becomes a massive gel with the green color of the nickel ion disappearing. The semi-solid product is washed several times with water to remove water-soluble matter and the washings are decanted. After the gel-like substance is removed, the resultant slushy solid is collected on a Buchner funnel and dried. The precipitated nickel obtained weighs 65–70 g, differing slightly according to the case, and contains about 10 g of nickel. The precipitated nickel can be stored in a moisture-free vessel. In all of the above procedures, tap water may be used for washing.

To obtain U–Ni–BA containing about 2 g of nickel, one-fifth of the above precipitated nickel is treated with sodium hydroxide solution. The dry precipitated nickel is added in small portions with vigorous stirring to a 1 l or larger three-necked round-bottomed flask equipped with a good stirrer and a thermometer, and containing 250 g of 20 % sodium hydroxide solution. As a violent reaction takes place with the evolution of hydrogen, the flask should be cooled in an ice bath with vigorous stirring to maintain the temperature at 50–55° C. Addition of the entire amount of precipitated nickel requires 10–15 minutes. Stirring is continued until the evolution of hydrogen ceases, with the occasional application of heat, if necessary, on a water bath to maintain the temperature at about 50° C. When the reaction is complete, the mixture is left standing for a few minutes to allow the black particles to settle (Note 4), and the upper liquor is decanted. The black matter is transferred to a 100 ml beaker with distilled water and washed with 200 ml of warm distilled water divided into several portions. At the end of this operation, the wash-water should be neutral to phenolphthalein. The solid is washed with the solvent to be used for the hydrogenation, e.g., ethanol, and transferred to the reduction vessel.

Notes: 1) The wide-necked round-bottomed flask may be replaced by a beaker.

2) The temperature can be conveniently regulated by using a hot water bath and an ice-water bath alternately.

3) If no heat is applied at the end of the reaction, the green color will not disappear and a catalyst of high activity can not be produced. At this stage, the mixture may safely be heated to 90–100° C.

4) Fine particles will not settle easily. Therefore, the supernatant

liquor, should be removed by decantation while still turbid, as long contact with alkali reduces catalytic activity.

4. 1. 9. U–Ni–AA

U–Ni–AA is a catalyst prepared by treating with acetic acid the precipitated nickel obtained from nickel chloride solution and aluminum grains. The precipitated nickel is usually obtained in the same way as U–Ni–BA.

As aluminum reacts with acetic acid very slowly, special techniques, such as the addition of an appropriate inorganic salt, are required to promote the reaction. It is suggested that 40 % acetic acid saturated with sodium chloride is most advisable for practical purposes.

In acetic acid treatment, in contrast to alkali treatment, nickel precipitated on the surface of aluminum grains, does not separate from the latter, thereby preventing the aluminum grains from dissolving away. Therefore, the remaining aluminum grains can act as a carrier for the catalyst; this makes U–Ni–AA particularly appropriate for vapor-phase hydrogenation.[26]

Preparation 18: U–Ni–AA

An 80 ml nickel chloride solution made from 32 g of $NiCl_2 \cdot 6H_2O$ crystals is heated to 50–60° C and is added with stirring to 60 g of aluminum grains (45 mesh) mixed with a small amount of water. An ion-exchange reaction takes place, and nickel begins to deposit onto the surface of the aluminum. The reaction is controlled by occasional cooling or heating either with cold or hot water (Note 1). The precipitated nickel is washed with cold water and 385 ml of 40 % acetic acid (70° C) containing 89 g (Note 2) of sodium chloride is added. After 3 to 7 minutes standing, the acid is decanted and the residue is washed with about 2 l of water (50–60° C), and then with an appropriate amount of ethanol. The catalyst contains 8 g of nickel.

Notes: 1) The precipitated nickel is usually prepared by a procedure similar to Preparation 17, but the preparation of U–Ni–AA for vapor-phase reduction requires the aluminum grains to be of somewhat larger mesh, and the concentration of nickel chloride solution to be the same as in Preparation 15.

2) The amount of sodium chloride required to saturate this volume of 40 % acetic acid.

4. 2. Urushibara Cobalt Catalysts

The preparative methods for Urushibara nickel catalysts can be applied without modification to the preparation of Urushibara cobalt catalysts, except that nickel chloride is replaced by cobalt chloride.[34] Just as in the nickel catalysts, U–Co–B and U–Co–A are obtained from cobalt chloride with zinc dust; U–Co–BA is prepared using aluminum grains instead of zinc dust. As the atomic weights of cobalt and nickel are almost the same, the quantities described in the preparations of Urushibara nickel catalysts can be employed without alteration.

Preparation 19: U–Co–B

A 10 ml hot aqueous solution (90–100° C) containing 4.04 g of cobalt chloride ($CoCl_2 \cdot 6H_2O$) is added all at once with vigorous stirring to a hot mixture (90–100° C) of zinc dust (10 g) and water (4 ml) placed in a 100 ml flask on a boiling water bath. The reaction product (precipitated cobalt) is transferred to a 300 ml beaker and washed with 200 ml of hot water. After 160 g of 10 % sodium hydroxide solution has been added, the mixture is heated at about 50–55° C on a water bath for 15 minutes with occasional stirring. The supernatant liquor is then decanted and the residue is washed with two 100 ml portions of hot water, and then with two 50 ml portions of ethanol. About 6.5–7 g of catalyst, containing cobalt (ca. 1 g), zinc, zinc oxide, and a trace amount of alkali is obtained.

Preparation 20: U–Co–A

The precipitated cobalt obtained in Preparation 19 is treated with 160 ml of 13 % acetic acid. The mixture is stirred for approximately 5 minutes until the evolution of hydrogen ceases and a solid rises to the surface of the solution, which in turn develops a pink color. To obtain an active catalyst, the coloration stage is indispensable. The solid is collected on a sintered glass filter and washed with 200 ml of hot water, then with 100 ml of ethanol. About 1–1.2 g of catalyst, containing about 0.8 g of cobalt together with small quantities of zinc and zinc oxide, is obtained.

Preparation 21: U–Co–CB

Similar to Preparation 7 (U–Ni–CB), except that the nickel chloride is replaced by cobalt chloride ($CoCl_2 \cdot 6H_2O$), the weight being the same.

Preparation 22: U–Co–CA

Similar to Preparation 8 (U–Ni–CA), except that nickel chloride is replaced by cobalt chloride, and the volume of 10 % acetic acid is changed to 150 ml. The precipitated cobalt can also be prepared from 4.04 g of cobalt chloride $CoCl_2 \cdot 6H_2O$ and 10 g of zinc dust as in Preparation 7.

Preparation 23: U–Co–B(s)

U–Co–B(s) is a U–Co–B catalyst prepared from crystalline cobalt chloride and zinc dust by a simplified method.[37] To a mixture of zinc dust (5 g) and water (1 ml) placed in a 50 ml beaker, add 2.02 g of commercial cobalt chloride crystals, $CoCl_2 \cdot 6H_2O$, (corresponding to 0.5 g of cobalt). The mixture is stirred well with a glass rod. A mild exothermic reaction begins to take place and the mixture becomes slushy in about 5 minutes. The precipitated cobalt is washed with 100 ml of cold water, and the washing water is removed by filtration or decantation. The precipitated cobalt is transferred to a 200 ml beaker and heated for 15 minutes at 50° C on a water bath with 80 g of 10 % sodium hydroxide solution. The supernatant liquor is decanted, and the remaining solid is washed twice with 50 ml of warm purified water, then twice with the same amount of ethanol.

Preparation 24: U–Co–A(s)

The precipitated cobalt (corresponding to 0.5 g of cobalt) prepared by Preparation 23 from cobalt chloride crystals is placed in a 200 ml beaker to which 75 ml of 15 % acetic acid is added, and the mixture is stirred at room temperature. In several minutes, the evolution of hydrogen ceases and a black solid comes to the surface of the solution, which becomes pink. The solid is collected on a sintered glass filter and washed with 200 ml of cold water, then with 100 ml of ethanol.

Preparation 25: U–Co–A(s) (HCl)

Precipitated cobalt (Preparation 23), corresponding to 0.5 g of cobalt, is placed in a 500 ml beaker, and stirred at room temperature with 200 ml of 0.75 N hydrochloric acid. Stir well to prevent the vigorous evolution of hydrogen, which tends to get out of control. Within one minute, a black solid comes to the surface of the solution, which becomes pink. At this stage, the solid is collected immediately on a sintered glass filter and washed with 200 ml of cold water, then with 100 ml of ethanol.

Preparation 26: U–Co–BA

Similar to Preparation 15 (U–Ni–BA), except that the materials are 10 g of aluminum grains (40–80 mesh) and 8.08 g of cobalt chloride crystals ($CoCl_5 \cdot 6H_2O$). The U–Co–BA thus prepared contains about 2 g of cobalt.

4. 3. Urushibara Copper Catalysts

In analogy with U–Ni–A and U–Co–A, precipitated copper is prepared from a copper(II) chloride solution and zinc dust, and is treated with acetic acid. The product is the Urushibara copper catalyst.[34] As precipitated copper hardly reacts with sodium hydroxide solution, U–Cu–B (an Urushibara copper catalyst obtained by alkali treatment) is practically useless.

Preparation 27: U–Cu

To a hot mixture (90–100° C) of zinc dust (10 g) and water (5 ml) placed in a 200 ml flask, 10 ml of a hot aqueous solution (90–100° C) containing 2.69 g of copper(II) chloride ($CuCl_2 \cdot 2H_2O$) is added all at once with vigorous stirring. The reaction terminates almost instantaneously. The supernatant liquor is decanted and the solid (precipitated copper) is transferred to a 300 ml beaker and washed with 200 ml of hot water. It is then treated for some 30 minutes with 160 ml of 13 % acetic acid at 70–75° C on a water bath and the supernatant liquor is decanted. The solid is washed with two 100 ml portions of hot water, then with two 50 ml portions of ethanol. About 2–2.5 g of black catalyst, containing copper (about 1 g) and zinc, is obtained. Urushibara copper catalyst is black before it is used for hydrogenation, but changes to red-brown after use.

Preparation 28: U–Cu–C

In a 100 ml flask, 10 g of zinc dust and 10 ml of water are placed. This is cooled well with ice and 30 ml of cold aqueous solution containing 2.69 g of copper(II) chloride ($CuCl_2 \cdot 2H_2O$) is added by drops during a 10 minute period with vigorous stirring. The precipitated copper is transferred to a 300 ml beaker and washed with 200 ml of cold water. It is then treated at room temperature with 160 ml of 13 % acetic acid for two hours. The supernatant liquor is decanted and the residual solid is washed with two 100 ml portions of cold water, then with two

50 ml portions of ethanol. About 3–4 g of black catalyst, containing copper (about 1 g) and zinc, is obtained.

Preparation 29: U–Cu–C (Modified Method)

The preceding method (Preparation 28) requires a rather long digestion time. Therefore, a modified method was devised to reduce the preparation time in which the precipitated copper is produced with ice-cooling, and digestion is carried out with heating.[37]

The precipitated copper (Preparation 28) is treated for about 20 minutes with 200 ml of 20 % acetic acid at 80–90° C on a boiling water bath. At the end of this procedure, a solid comes up to the surface of the solution. It is collected on a sintered glass filter and washed with 200 ml of water, then with 150 ml of ethanol. About 2.3–2.5 g of bulky catalyst, containing copper (about 1 g) and zinc, is obtained.

4. 4. Urushibara Iron Catalysts

Paul and Hilly have produced a Raney iron catalyst by analogy with Raney nickel.*1) It is widely recognized that this catalyst has a striking specificity for the partial hydrogenation of acetylenic compounds to ethylenic compounds. However, iron-aluminum alloy is prepared in a chemical laboratory with great difficulty, which precludes the handy use of the catalyst.

Iron particles prepared by the Urushibara method proved to have catalytic activity, and a new iron catalyst, comparable to Raney iron, has been established.[38] As the difference between the electrode potentials of zinc and iron is smaller than the difference between those of zinc and nickel, cobalt, or copper, the reduction of iron(II) or (III) chloride solution by zinc dust takes place very slowly. Crystals of iron(III) chloride, however, react vigorously with a mixture of zinc dust and water (see Preparation 9), and, on acetic acid treatment, a fine grayish black solid is obtained. Iron(II) chloride crystals, on the other hand, react with zinc dust less vigorously, and external heating is advisable. From the latter, on acetic acid treatment, a fine brownish black solid is obtained. Both products are good catalysts. These are referred to as U–Fe(III) and U–Fe(II), respectively. The Roman numerals in parentheses stand for the original valences of the iron in

*1) P. Paul and G. Hilly, *Bull. Soc. Chim. France* [5] **6**, 218 (1939); A. F. Tompson and S. B. Wyatt, *J. Amer. Chem. Soc.*, **62**, 2555 (1940).

the chloride. Both catalysts consist of zinc and iron, but the former is somewhat bulkier and contains a larger amount of zinc.

Tiny amounts of contamination metals in Urushibara iron catalyst, such as nickel or cobalt, act as a kind of promoter, and produce a favorable effect on the activity of the catalyst.

As in the preparation of U–Ni–BA, aluminum grains have also been used in the place of zinc dust for the preparation of the precipitated iron. The iron(III) chloride reacted vigorously with aluminum grains to give precipitated iron. However, U–Fe–BA, similarly obtained by treatment of this precipitated iron with a sodium hydroxide solution, proved to have no catalytic activity.

Preparation 30: U–Fe(III)

To well mixed zinc dust (25 g) and water (8 ml) in a 50 ml beaker, 9.68 g (corresponding to 2 g of iron) of commercial iron(III) chloride crystals ($FeCl_3 \cdot 6H_2O$) is added. The mixture is stirred well with a glass rod. Immediately a vigorous exothermic reaction takes place, but subsides in a short time (about 10 seconds). To complete the reaction, the mixture is stirred further until the color of the iron(III) ion disappears. The product (precipitated iron) is washed with 400 ml of cold water, and the washing water is removed by filtration or decantation. It is then treated at 60–70° C with 330 g of 15 % acetic acid for about 20–25 minutes with occasional stirring. At the end of this operation the evolution of hydrogen subsides and a black solid, which floats due to the adhering hydrogen bubbles, comes to the surface of the almost colorless solution. The solid is collected quickly on a sintered glass filter and washed with 300 ml of cold water, then with 100 ml of ethanol. The catalyst is a grayish black solid and contains a small amount of zinc.

Preparation 31: U–Fe(II)

Commercial iron(II) chloride crystals ($FeCl_2 \cdot nH_2O$), corresponding to 2 g of iron (Note 1), are added to a mixture of zinc dust (20 g) and water (6 ml) placed in a 50 ml beaker. The mixture is heated on a boiling water bath and stirred for about 2 minutes with a glass rod. The product (precipitated iron) is washed with 300 ml of cold water, and the washing water is removed by filtration or decantation. It is then treated at 60–70° C with 300 g of 15% acetic acid for 15–20 minutes with occasional stirring, until the evolution of hydrogen subsides, and a solid comes to the surface of the almost colorless solution. For suc-

ceeding operations, consult Preparation 30. The catalyst is a bulky brownish black solid, containing about 2 g of iron and a considerable amount of zinc.

Note: 1) Commercial iron(II) chloride contains iron in an indefinite proportion. The iron content should be determined by analysis.

Preparation 32: U–Fe(III)–Ni (Fe 1 : Ni 0.01)

Similar to Preparation 30, except that 0.2 ml of nickel chloride solution (10 ml of which correspond to 1 g of nickel) is added to the mixture of zinc dust and water, before the iron(III) chloride crystals are added.

Preparation 33: U–Fe(II)–Ni (Fe 1: Ni 0.01)

Similar to Preparation 31, except that 0.2 ml of nickel chloride solution (10 ml of which correspond to 1 g of nickel) is added to the original mixture of zinc dust and water, before the iron(II) chloride crystals are added.

Preparation 34: U–Fe(II)–Co and U–Fe(III)–Co (Fe 1: Co 0.025)

Similar to Preparations 32 and 33 (U–Fe–Ni), except that 0.5 ml of cobalt chloride solution (10 ml of which corresponds to 1 g of cobalt) replaces 0.2 ml of nickel chloride solution.

Preparation 35: U–Fe(III)–BA

To a mixture of 10 g of aluminum grains (Note 2) (40–80 mesh) and 20 ml of water placed in a 300 ml beaker, 9.68 g of iron(III) chloride crystals, $FeCl_3 \cdot 6H_2O$, (corresponding to 2 g of iron) is added, and stirring is started at the same time. Heat is liberated as the crystals dissolve, and the mixture should be cooled with water to prevent the reaction from getting out of control (Note 3). The reaction gradually subsides with the fading away of the color of the iron(III) ion. In this period, the mixture should be heated occasionally on a water bath to maintain the reaction temperature at 45–55° C. In about 10 minutes the color almost disappears, but the exothermic reaction continues, and the temperature finally rises to approximately 60° C. After about 15 minutes from the beginning of the reaction, the product is washed with 200 ml of water and the washing water is removed by decantation.

The precipitated iron is mixed with 10 ml of water, and 250 g of

20 % sodium hydroxide solution is added in small portions. As a vigorous reaction occurs on every addition of alkali, vigorous stirring is required to prevent the running over of the solution, and every addition should wait until the preceding reaction subsides. In successive additions, the amount of alkali may be increased gradually, but the temperature should be controlled by cooling with water so that it does not exceed 55° C. Addition of the first half of the alkali requires 15–20 minutes. The other half may be added all at once, and the mixture is stirred carefully to keep the temperature from exceeding 55° C. The evolution of hydrogen ceases about 40 minutes after the beginning of the reaction. The remaining solid is collected on a sintered glass filter and washed with 300 ml of water, then with an appropriate amount of ethanol. This is the U–Fe(III)-BA catalyst, and it is ready for use in reduction. Dry weight is about 1.8 g.

Notes: 2) It is advisable to clean the aluminum grains in advance with 3% sodium hydroxide solution or 6 N hydrochloric acid (see Preparation 15 or 17).
3) If the mixture is stirred without cooling, the temperature rises abruptly as soon as the crystals begin to dissolve, and the solution is apt to overflow.

4. 5. Regeneration of the U–Ni–A Catalyst

Waste U–Ni–A or U–Ni–B, once used for hydrogenation, may be regenerated by a very simple operation, and they may be used repeatedly as active catalysts.[36]

Spent catalyst is recovered by filtration, dried at about 100° C, and stored. Regenerated catalyst is produced using spent catalyst in place of the precipitated nickel. The spent catalyst is mixed with zinc dust and a small amount of water, and then 13 % acetic acid is added, whereupon a reaction takes place with the evolution of hydrogen, the solution becoming green. The black solid is collected and washed with distilled water. This is the regenerated U–Ni–A, which has a recovered activity. Digestion at 50–55° C with 10 % sodium hydroxide solution instead of acetic acid gives a regenerated U–Ni–B catalyst, but the activity is very much lower than that of fresh catalyst, and the latter process is not recommended.

As recovered U–Ni–B catalyst still cotains a large amount of zinc, it may be treated with 13 % acetic acid without further addition of

zinc dust. In this case, U–Ni–A is reproduced with the evolution of hydrogen.

It appears that a large amount of zinc is not necessary even in the regeneration of U–Ni–A. Moreover, an active U–Ni–A catalyst is still regenerated when the used U–Ni–A, as it stands, is heated with an appropriate amount of 10–20 % acetic acid at 70–75° C for about one minute. In this case, the spent catalyst reacts with acetic acid violently and the solution becomes green; a black solid, which floats, due to the adhering hydrogen bubbles, comes to the surface of the solution. The regenerated catalyst is still active, but a considerable loss of nickel is observed, owing to the dissolution of nickel by acetic acid. Therefore, the regeneration is necessarily accompanied by loss of quantity.

The activities of the catalysts regenerated by these methods are somewhat lower compared with that of freshly prepared U–Ni–A catalyst, but they are sufficiently high for the usual reductions.

Directions for regeneration of the U–Ni–A catalyst and the activities of regenerated catalysts are to be found in Section 6. 4. 2(*c*).

5. Characteristics of the Catalysts

There are many varieties of Urushibara catalyst. Each individual Urushibara catalyst has its own characteristics, and can be used in accordance with the properties of the substance to be reduced. Much effort has been devoted to the elucidation of the origin of the intrinsic properties and characteristic activities of Urushibara catalysts.

The preparation of the Urushibara catalysts consists of two steps. The first is the preparation of precipitated metals; the second, the digestion of the precipitated metals with acid or alkali. Modifications of these two steps determine the nature of the Urushibara catalyst obtained.

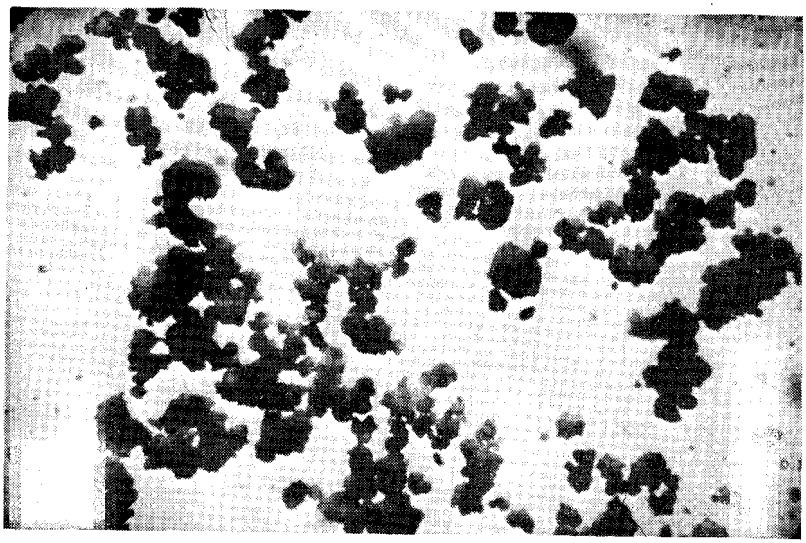
5. 1. Appearances and Microphotographs

(a) U–Ni–A and U–Ni–B

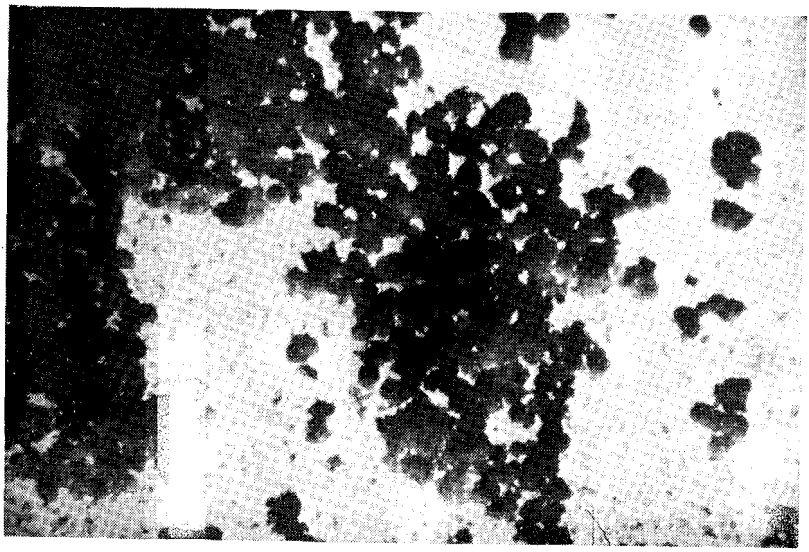
U–Ni–A and U–Ni–B are the Urushibara catalysts which are most frequently used. They are produced by digesting the precipitated nickel, which is obtained from hot nickel chloride solution and zinc dust, with acetic acid or sodium hydroxide solution.

The precipitated nickel is a grayish solid of considerable bulk, slushy when wet and a coarse powder when dry. U–Ni–B, prepared from this precipitated nickel by heating with 10 % sodium hydroxide solution (Preparation 3) is a dark gray solid; U–Ni–A, prepared by heating with 13 % acetic acid (Preparation 4) is a black powder. They differ greatly in appearance. A comparison of these catalysts, both prepared from 4.04 g of $NiCl_2 \cdot 6H_2O$ (corresponding to 1 g of nickel), reveals that the former is far more bulky, the gross weight of dried catalyst being 6.5–7.5 g for the former and 1.1–1.4 g for the latter. The weight of the former amounts to as much as 10 g when the amount of alkali is reduced. U–Ni–A contains 0.8–0.85 g of nickel and the amount of contaminants, such as zinc and zinc compounds, is very low. In contrast, U–Ni–B contains large amounts of zinc and zinc oxide, which, however, act as carriers in hydrogenation.

U–Ni–A prepared from nickel acetate has a gross weight less than

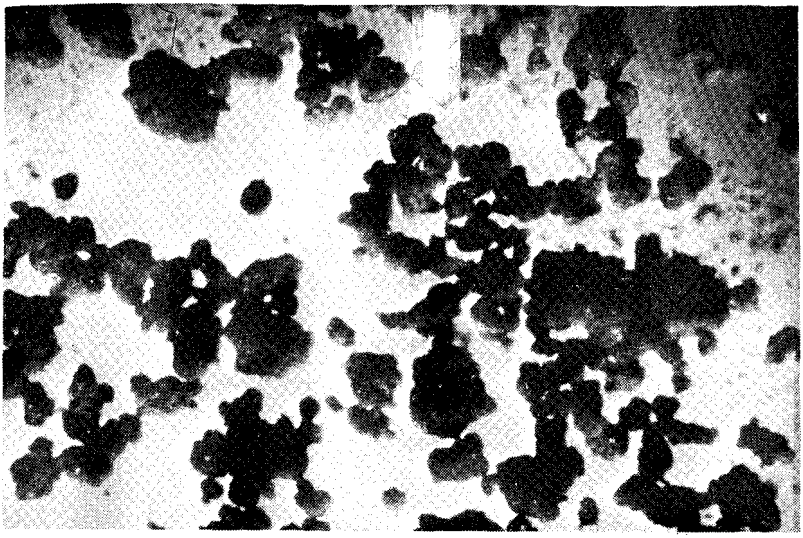


(a) Precipitated nickel ×250

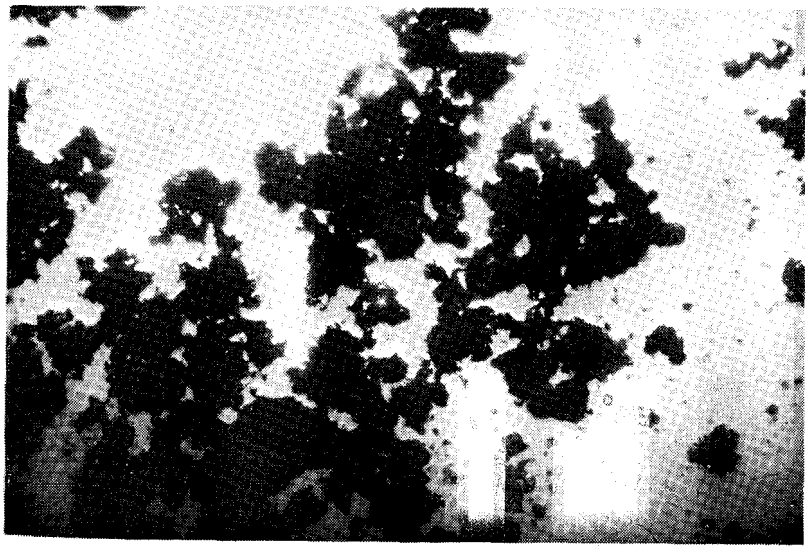


(b) Precipitated nickel prepared at a low temperature ×250

Fig. 5–1. Microphotographs of Precipitated

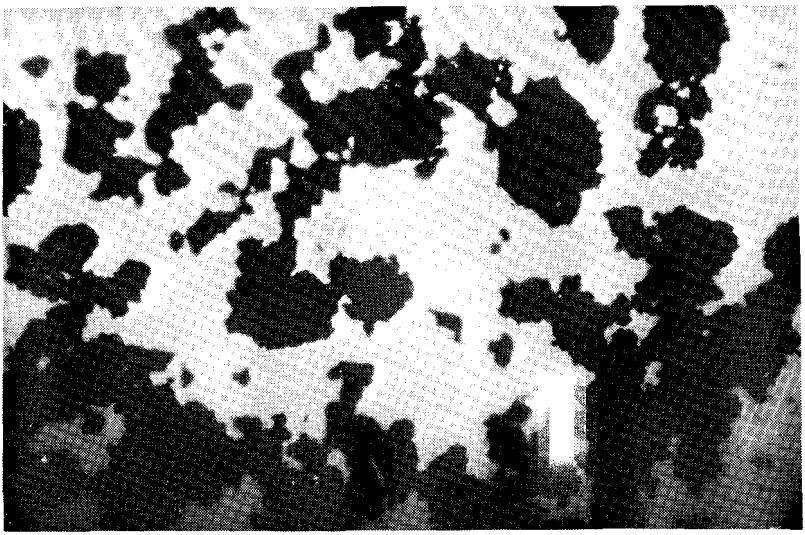


(c) Precipitated cobalt ×250

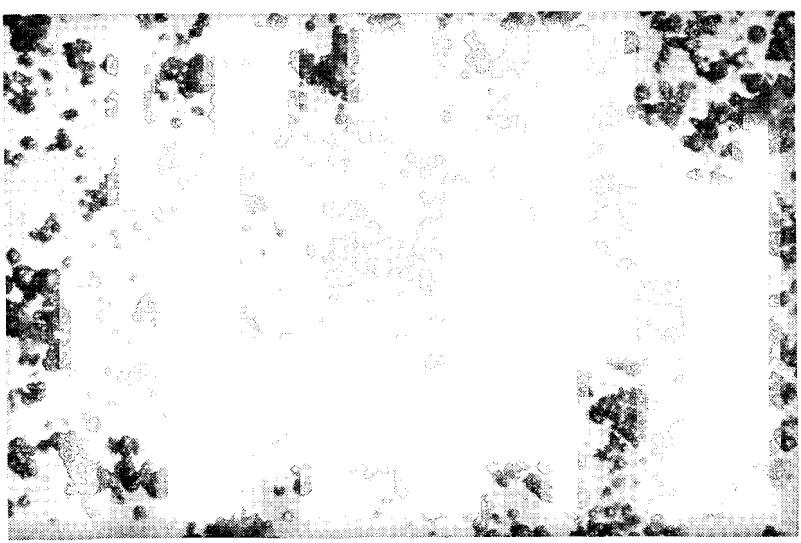


(d) *Precipitated copper* ×250

Metals (from Chloride Solutions)

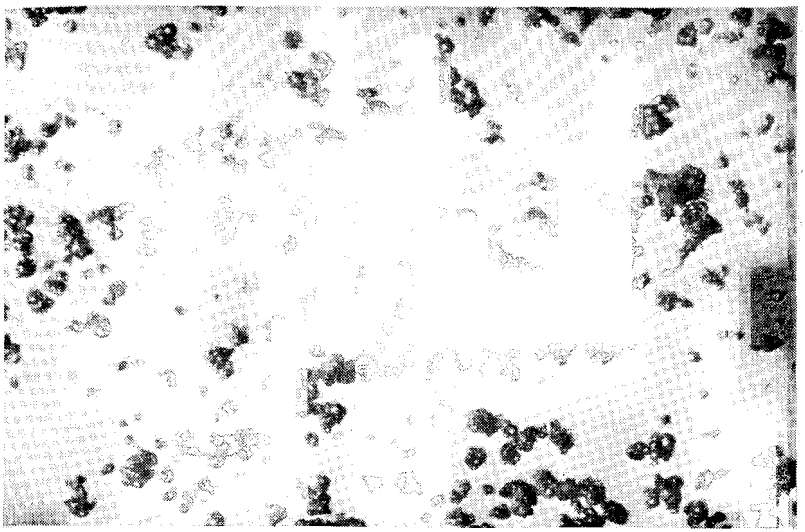


(e) Precipitated copper prepared at low temperature ×250



(f) Precipitated iron from iron(II) chloride ×150

Fig. 5–1. Continued



(g) Precipitated iron from iron(III) chloride ×150

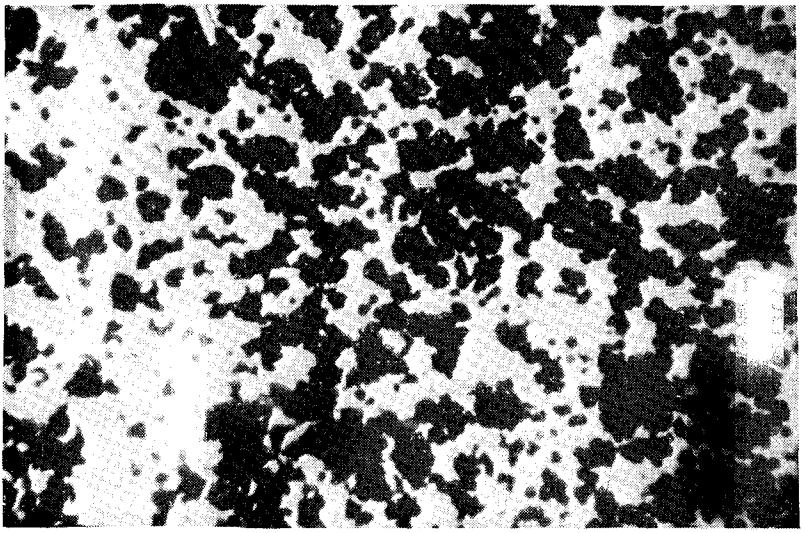
Fig. 5-1. Continued

that obtained from nickel chloride. However, U–Ni–B prepared from nickel acetate has a dry weight of about 8.5–10.5 g (for 1 g of nickel), and is about three times as bulky as the catalyst obtained from nickel chloride. Therefore, the former should contain still larger amounts of contaminants, such as zinc oxide, and this can be seen from microphotographs of these catalysts (Fig. 5–2).

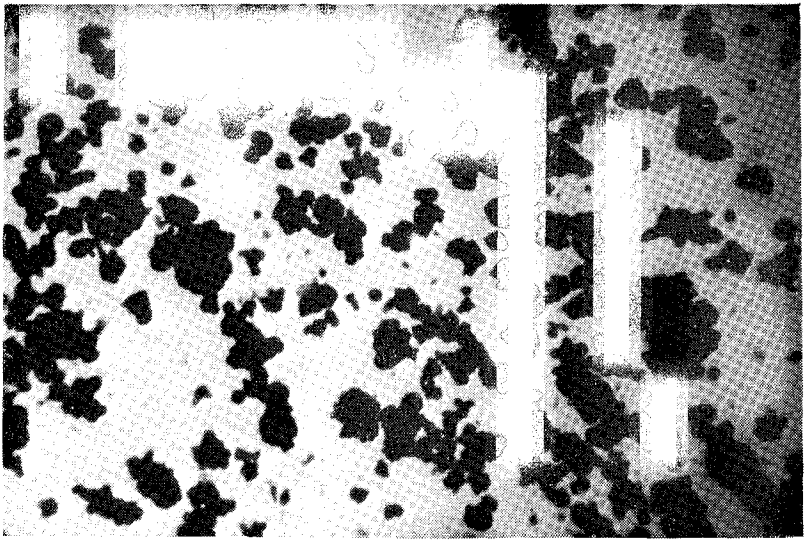
U–Ni–A(s), prepared by a simplified method in which precipitated nickel is produced from zinc dust and nickel chloride crystals in the presence of a small amount of water and then treated with acetic acid, has an appearance very similar to that of ordinary U–Ni–A, but the gross weight relative to a definite nickel content is usually somewhat less in the former.

(*b*) *U–Ni–BA*

U–Ni–BA is prepared by digestig precipitated nickel, obtained from aluminum grains and nickel chloride solution with 20 % sodium hydroxide solution. The nature of the precipitated nickel is a function of the size of the aluminum grains. Aluminum grains of 40–80 mesh give a grayish precipitated nickel, from which U–Ni–BA is obtained as a black powder. U–Ni–BA obtained from 4.04 g of nickel

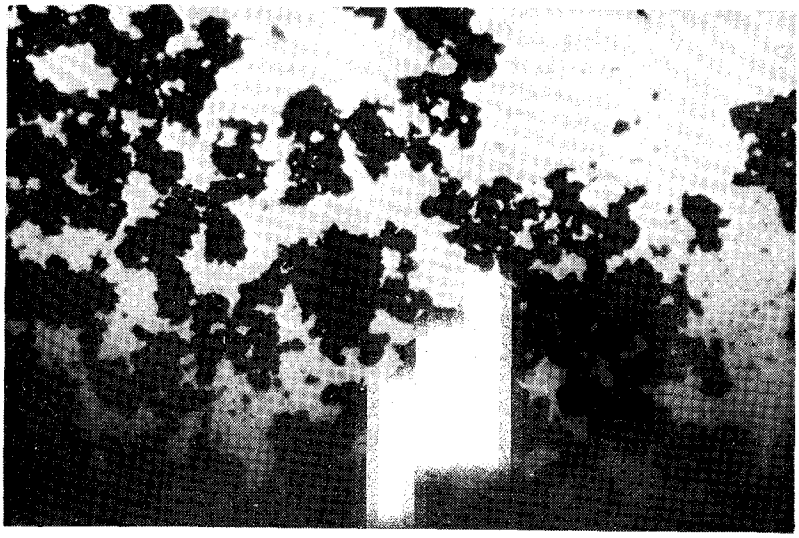


(a) U–Ni–A ×250

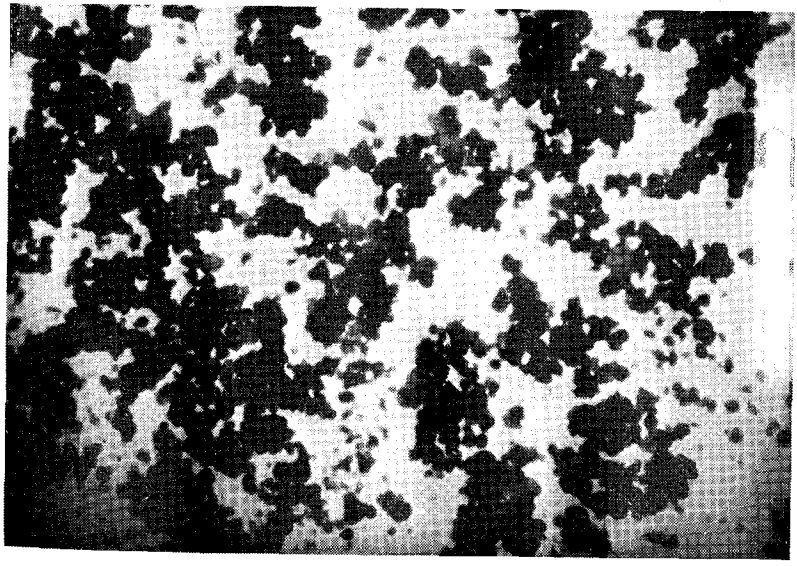


(b) U–Ni–B ×250

Fig. 5–2. Microphotographs

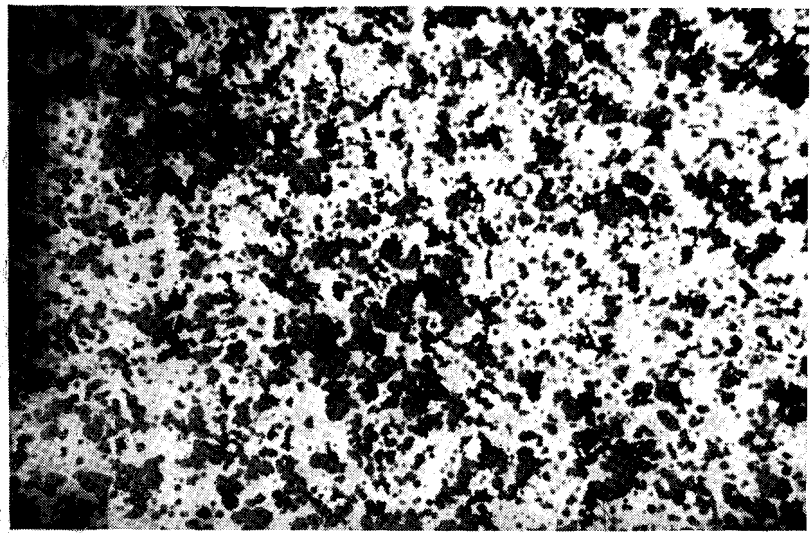


(c) U–Ni–A from nickel acetate ×250

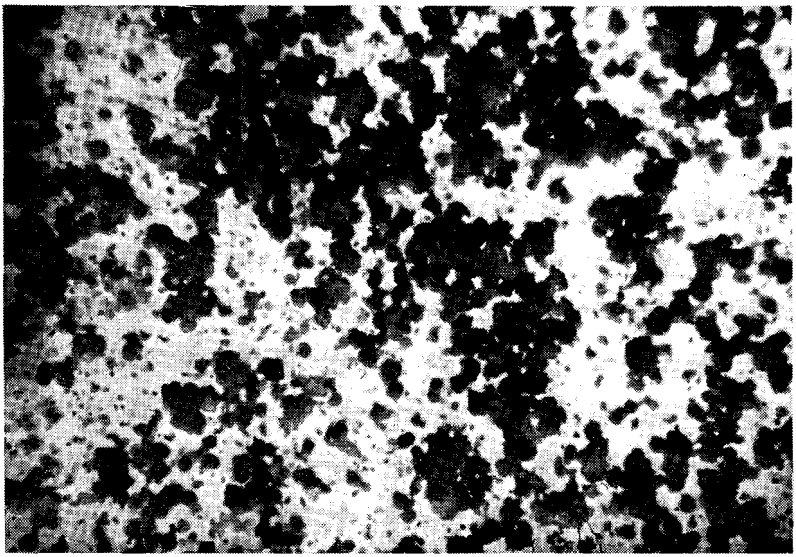


(d) U–Ni–B from nickel acetate ×250

of Urushibara Catalysts



(e) U–Ni–CA ×250



(f) U–Ni–CB ×250

Fig. 5–2. Continued

(g) U–Ni–BA ×250

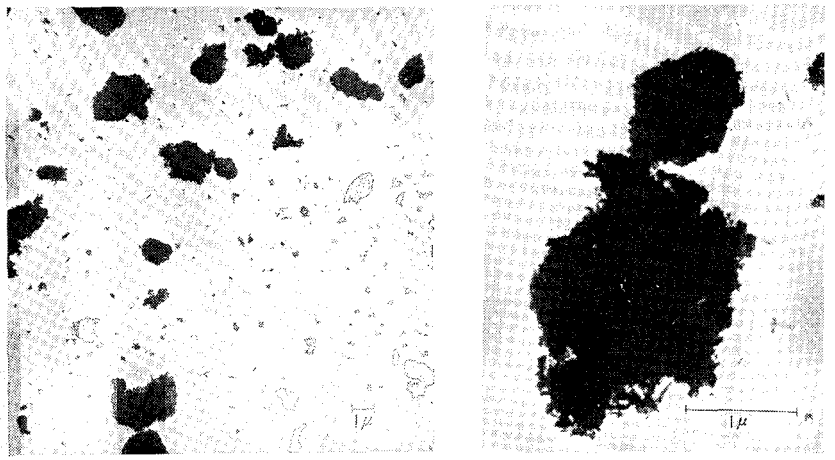
Fig. 5–2. Continued

chloride crystals has a dry weight of 1.4–1.8 g. Its appearance differs little from that of U–Ni–A, but the particle size is greater than that of either U–Ni–A or U–Ni–B. Microphotographs are shown in Fig. 5–2(g). X-ray diffraction patterns of U–Ni–BA and U–Ni–A also differ remarkably from each other, conforming to the difference in the natures of the catalysts.

According to an electron microscope observation of U–Ni–BA, the particle size of the catalyst covers a wide range, from 1/10 μ to several μ (Fig. 5–3(a)), but it seems that fine particles are produced primarily by the destruction of larger ones in the course of the preparation of the catalyst. An enlarged photograph (Fig. 5–3(b)) shows that the nickel crystallites form a mozaic assembly in globular form, a common characteristic of Urushibara catalysts prepared by way of the ion-exchange reaction.

(*c*) *U–Ni–AA*

U–Ni–AA is a catalyst prepared by treating precipitated nickel obtained from nickel chloride solution and aluminum grains with acetic acid solution. As aluminum grains do not dissolve in acetic acid alone, digestion should be carried out with 40 % acetic acid saturated with



(a) (b)

Fig. 5–3. Electron Microphotographs of U–Ni–BA

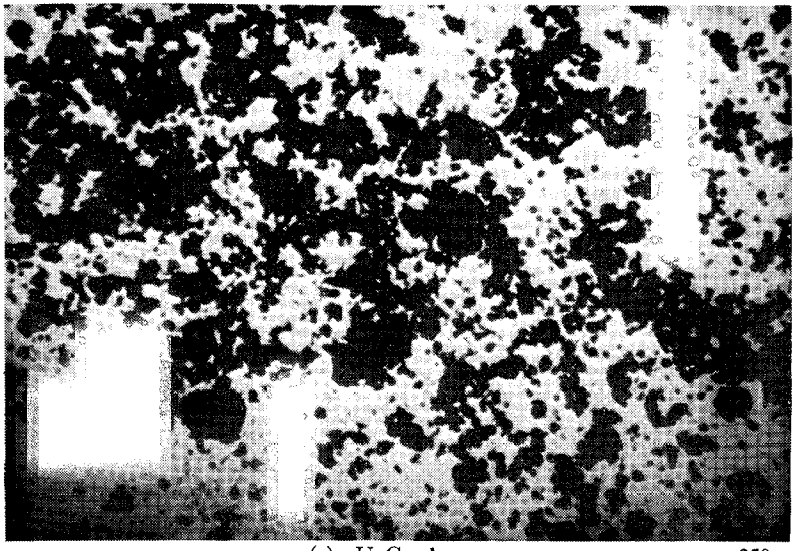
sodium chloride. Moreover, as nickel precipitated on aluminum grains will not separate from the latter during the acetic acid treatment, most of the aluminum remains undissolved and acts as a kind of carrier, supporting on its surface the real U–Ni–AA catalyst. The catalyst is, therefore, a black granular solid and is most appropriate for vapor-phase hydrogenation.

(*d*) *U–Ni–CA and U–Ni–CB*

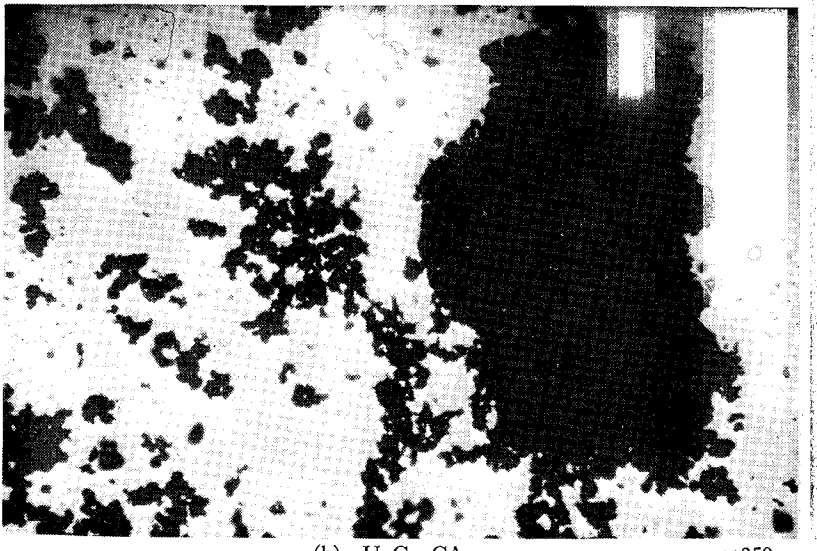
Precipitated nickel prepared at a low temperature leads to U–Ni–C catalysts. Under conditions similar to those used in the preparation of ordinary U–Ni catalysts, *e.g.*, with respect to the concentration of the nickel chloride solution or the amount of zinc dust added, the ion-exchange reaction takes place very slowly if conducted at room temperature or under cooling with water. In this case, nickel precipitates uniformly on the surface of the zinc dust particles, giving a very fine nickel precipitate (Fig. 5–1(b)). Treatment of this precipitated nickel with acid or alkali yields U–Ni–CA or U–Ni–CB, respectively. Hence, U–Ni–C catalysts have a finer particle size than ordinary U–Ni catalysts. This has been verified by microphotography (Figs. 5–2 (e), (f)).

(*e*) *U–Co and U–Cu*

U–Co and U–Cu are prepared by the acid or alkali treatment of

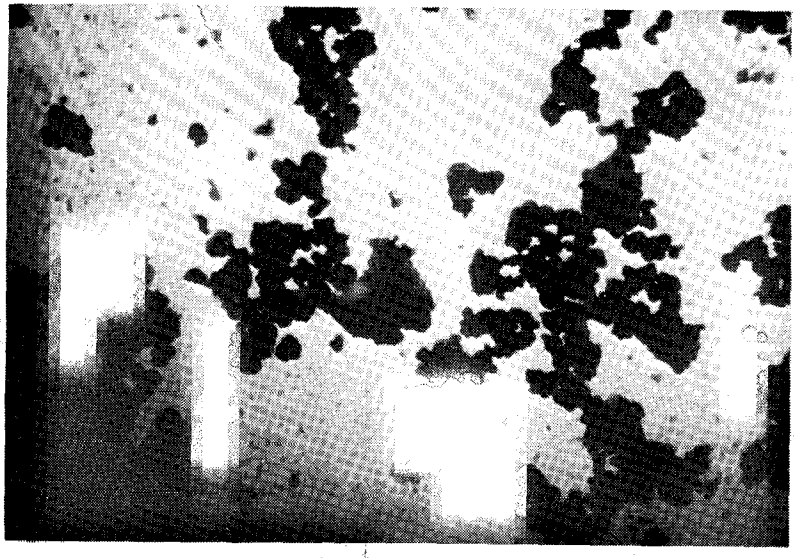


(a) U–Co–A ×250



(b) U–Co–CA ×250

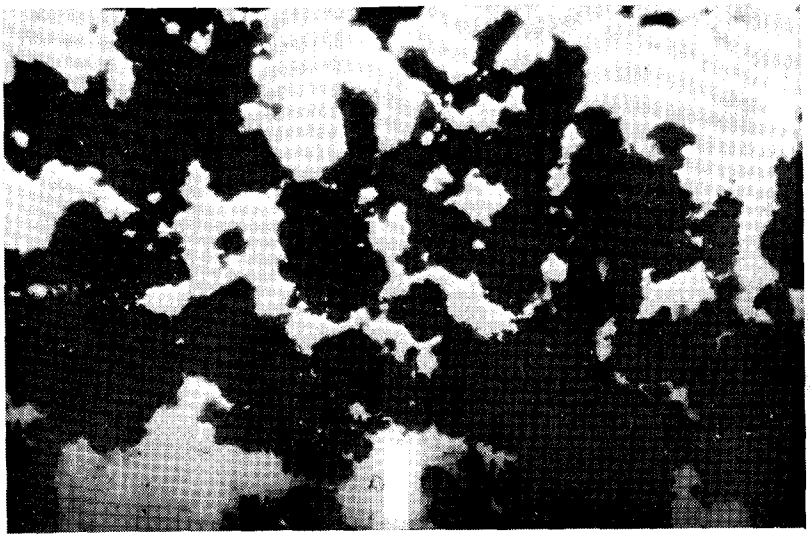
Fig. 5–4. Microphotographs of U–Co and U–Cu



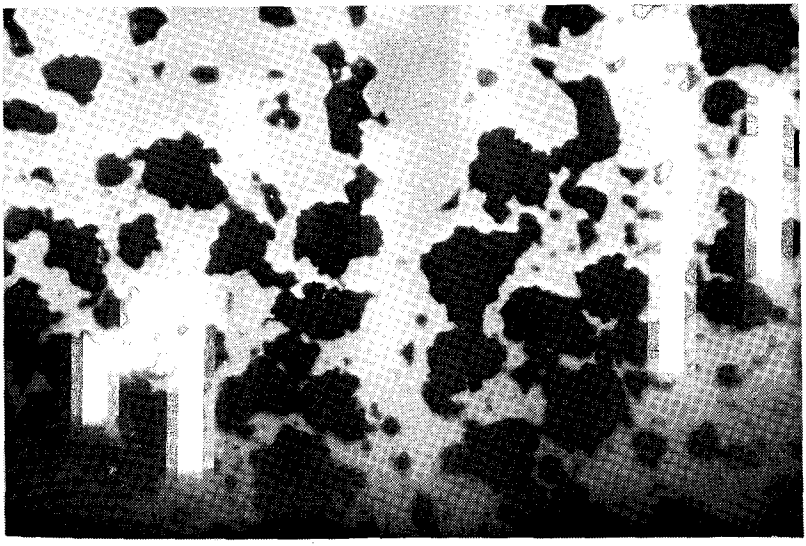
(c) U–Co–B ×250

(d) U–Co–CB ×250

Fig. 5–4. Continued



(e) U–Cu ×250



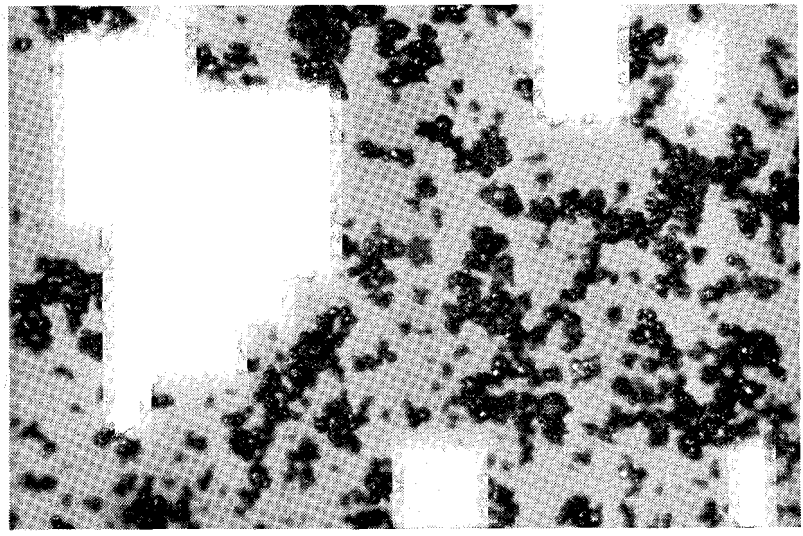
(f) U–Cu–C ×250

Fig. 5–4. Continued

precipitated cobalt or precipitated copper, obtained from zinc dust and cobalt chloride solution or copper(II) chloride solution, respectively. U–Co–A and U–Co–B have appearances very similar to those of the corresponding U–Ni catalysts. U–Co–A, obtained from 4.04 g of $CoCl_2 \cdot 6H_2O$ (corresponding to 1 g of cobalt), is a black powder weighing 1–1.2 g and contains about 0.8 g of cobalt together with very small amounts of zinc and zinc oxide. U–Co–B, obtained from the same amount of cobalt chloride, is a dark gray solid and is far more bulky than U–Co–A, weighing as much as 6.5–7 g and containing large amounts of zinc and zinc oxide together with a trace amount of alkali.

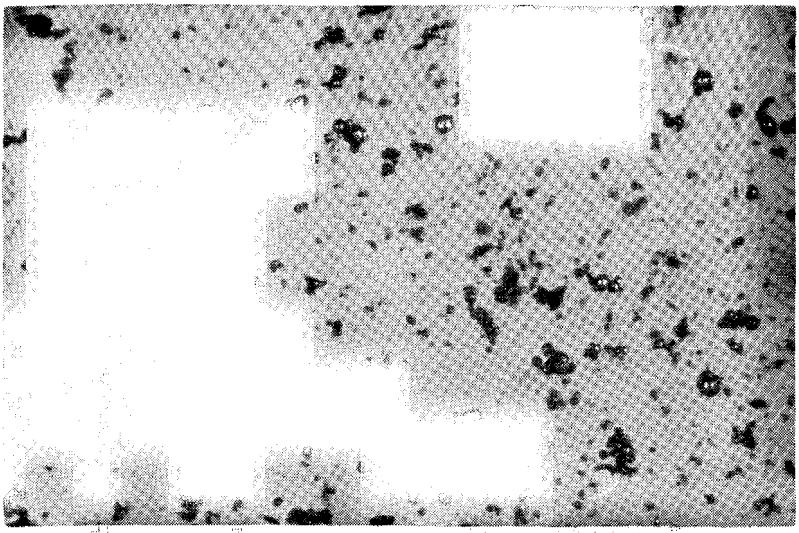
U–Cu catalyst is prepared by the acetic acid treatment of precipitated copper. The catalyst, corresponding to 1 g of copper, is a black powder weighing 2–2.5 g which turns reddish brown after use.

U–Co–C and U–Cu–C, prepared by a low temperature ion-exchange reaction, have smaller particle sizes than do ordinary U–Co and U–Cu. Microphotographs of these catalysts are shown in Fig. 5–4, together with those of U–Co and U–Cu; their parent materials, precipitated cobalt and precipitated copper, are shown in Fig. 5–1.

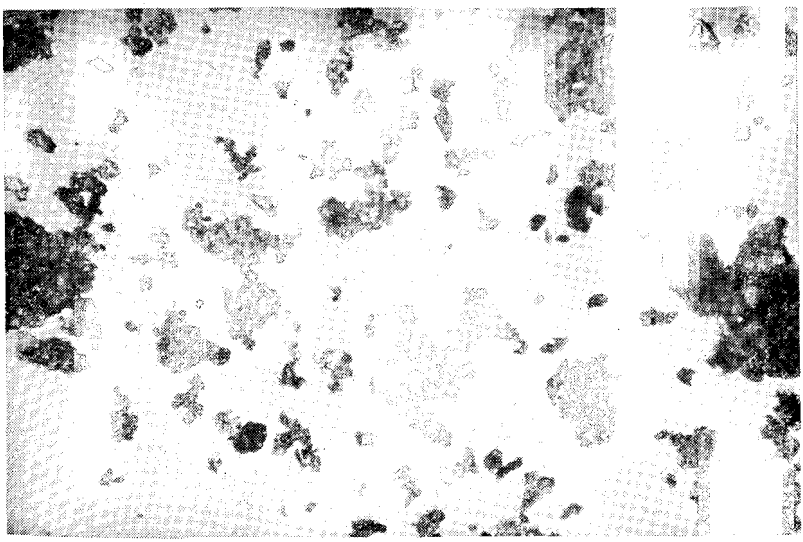


(a) U–Fe(II) ×150

Fig. 5–5. Microphotographs



(*b*) U–Fe–(III) ×150



(*c*) U–Fe(III)–BA ×150

of U–Fe Catalyst

(f) U–Fe

U–Fe(III) and U–Fe(II) are prepared by the acetic acid treatment of precipitated iron; precipitated iron from iron(III) chloride and zinc dust gives U–Fe(III), and that from iron(II) chloride and zinc dust gives U–Fe(II). U–Fe(III) is a fine grayish black solid, whereas U–Fe(II) is a fine brownish black solid; the gross weight of the catalyst corresponding to 2 g of iron is 2.2 g for the former and 4.6 g for the latter, though they are nearly equal in apparent bulk. U–Fe(II) probably contains more zinc than U–Fe(III). The microphotographs of both catalysts (Fig. 5–5) show that the grains of zinc dust are covered with iron, and that many spherical iron-zinc couples coagulate to form a block. Presumably the difference arises from the very nature of the precipitated iron, as the two catalysts are treated with acetic acid under nearly identical conditions. In fact, the precipitated iron obtained from iron(III) chloride is more easily eroded by acetic acid during digestion than that from iron(II) chloride. Therefore, in order to prepare U–Fe(III) containing a sufficient quantity of iron, the supernatant liquor should be drained off quickly as soon as digestion is complete.

5. 2. X-ray Diffraction Studies, Part I[13]

Powder X-ray diffractions of U–Ni–A, U–Ni–B, and precipitated nickel have been studied extensively. We shall present the results in the following, and compare Urushibara nickel with many of the nickel catalysts, *e.g.*, Raney nickel, nickel catalyst produced by thermal decomposition of nickel formate, and " reduced nickel catalyst " (powdered nickel produced by the reduction of nickel oxide). Based upon these results, and considering the electron diffraction results, which will be described later, we shall also discuss the activity of the Urushibara nickel catalyst, and consider what is responsible for this activity.

5. 2. 1. X-ray Diffraction Studies of Various Nickel Catalysts

The experiments presented here have been carried out using a self-recording X-ray diffractometer of the North American Philips Co. (Norelco). Powdered samples were mounted on flat holders and were rotated at a constant rate. The reflected X-ray beam was detected with a Geiger counter and the signals were amplified and recorded. The X-rays employed were Cu–K_α and the Bragg angle (2θ) was swept from 2° to 90°, which bracketed the spacing range of 22–1.09 Å. Pre-

cipitated nickel, Urushibara nickel, and nickel catalyst obtained from nickel formate were stored in ethanol after preparation, and filtered just before measurement. Wet specimens were mounted.

(*a*) *Nickel Powder Obtained from Nickel Carbonyl*

Figure 5–6 shows the diffraction pattern of powdered nickel prepared by the thermal decomposition of nickel carbonyl (mean particle size 0.1 μ). The abscissa is the Bragg angle 2θ, and the ordinate is the intensity of the diffracted X-rays (relative value). The relation

$$n\lambda = 2d \sin \theta$$

holds, where n is the order of diffraction, λ the wavelength of the X-rays used, d the spacing of the crystal plane, and θ the angle of the incident ray. Three sharp lines are observed as shown in Fig. 5–6. Their positions and intensities are:

2θ	44.50°	51.75°	76.25°
Intensity	100	54.1	33.7

The intensities are relative to the most intense line, which is taken to be 100.

These agree well with the values of face-centered cubic nickel (cf. Table 5–9 in Section 5. 3. 1), and it has been ascertained that nickel obtained from nickel carbonyl has this structure.

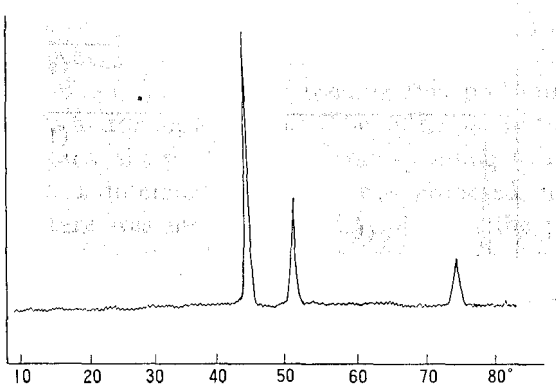


Fig. 5–6. X-ray Diffraction of Nickel Powder Prepared by Thermal Decomposition of Nickel Carbonyl

(*b*) *Precipitated Nickel*

Figure 5–7 (a) shows the diffraction patterns of precipitated nickel prepared from nickel chloride and zinc dust. The diffraction patterns of zinc and zinc oxide are separately illustrated in Fig. 5–7 (b) and (c). Comparing these figures, it is found that large amounts of zinc and zinc oxide are contained in the precipitated nickel.

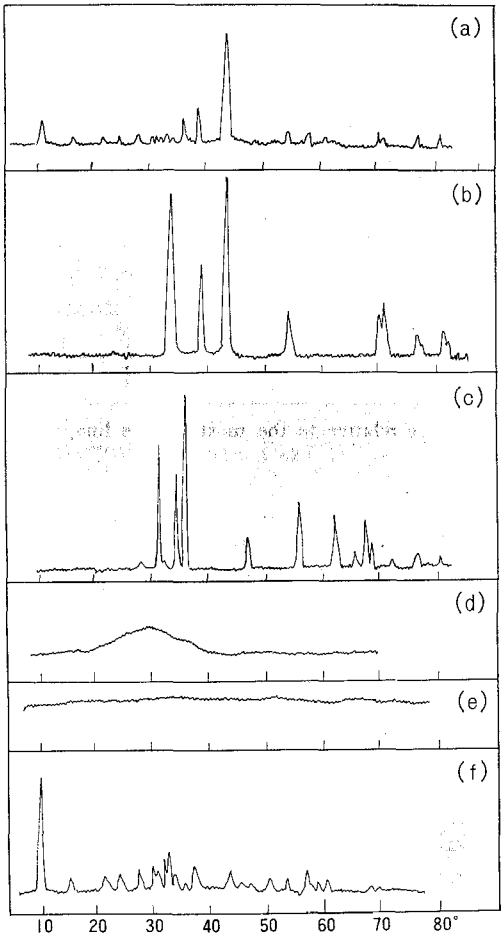


Fig. 5–7. X-ray Diffraction of Precipitated Nickel and Related Materials

(a) precipitated nickel; (b) zinc; (c) zinc oxide; (d) zinc hydroxide (colloidal); (e) nickel hydroxide (colloidal); (f) zinc hydroxide chloride.

Those lines in Fig. 5–7 (a) which were not attributable to these contaminants were found to be due to zinc hydroxide chloride Zn(OH)Cl. For the sake of comparison, the diffraction patterns of zinc hydroxide, nickel hydroxide, and zinc hydroxide chloride are shown in Figs. 5–7 (d), (e), and (f).

It is strange to find that nothing remains if the diffraction lines due to zinc, zinc oxide, and zinc hydroxide chloride are eliminated from the diffraction pattern of the precipitated nickel—in other words, lines corresponding to nickel metal (76.50°, 51.90°, 44.58°) are not present in the spectrum. It should be remembered that 10 % or more nickel is contained in the precipitated nickel.

(*c*) *Urushibara Nickel*

Catalytic activity is produced when precipitated nickel is digested at 55° C with 10 % sodium hydroxide solution. Fig. 5–8 (a) shows the diffraction pattern of U–Ni–B, which exhibits lines corresponding to zinc and zinc oxide, but no lines corresponding to zinc hydroxide chloride. Therefore, any zinc hydroxide chloride must be eliminated from the precipitated nickel during the treatment with 10 % sodium hydroxide solution.

The diffraction pattern of U–Ni–B shows no lines associated with nickel metal, although 20 % or more nickel is present. At first, it was supposed that the nickel was covered by a great amount of zinc, and that the diffraction lines were due only to the latter. This supposition was soon disproved by the following experiment: About 3 g of zinc dust mixed with a small amount of nickel (0.5 g), which was prepared in advance by the thermal decomposition of nickel carbonyl, was added to a nickel chloride solution to produce precipitated nickel. A special U–Ni–B was prepared by treating this precipitated nickel with 10 % sodium hydroxide solution. The diffraction of this U–Ni–B (Fig. 5–8 (b)) clearly shows three lines corresponding to nickel (Fig. 5–6). Therefore, a different explanation was proposed, namely that the crystal structure was insufficiently developed in the precipitated nickel.

U–Ni–NH_3 is a fairly active catalyst produced by treating precipitated nickel with 10 % aqueous ammonia, instead of sodium hydroxide solution. The diffraction pattern of this catalyst is shown in Fig. 5–8 (c), where no lines due to nickel are seen. It does, however, show lines due to zinc, zinc oxide, and zinc hydroxide chloride, together with new unidentifiable lines at 40.8°, 27.2°, 20.95°, and 20.3°, which were

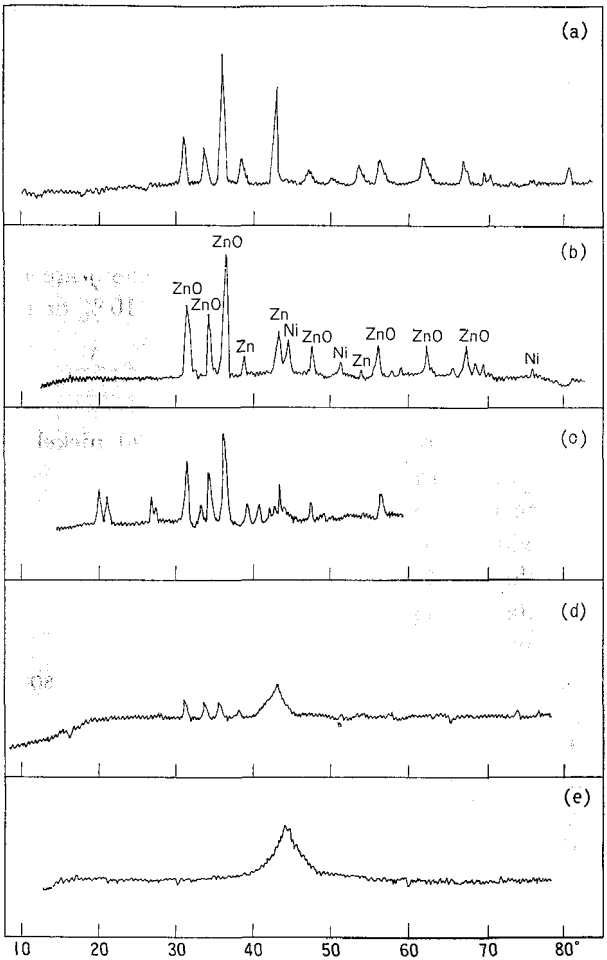


Fig. 5–8. X-ray Diffraction of U–Ni Catalysts

(a) U–Ni–B; (b) U–Ni–B (prepared from a source material containing nickel powder obtained by thermal decomposition of nickel carbonyl); (c) U–Ni–NH_3; (d) U–Ni–B (prepared by thorough treatment of precipitated nickel with 20% NaOH); (e) U–Ni–A

absent before ammonia treatment. We see that zinc hydroxide chloride is not completely removed, and also that a new compound is formed during ammonia treatment.

We have supposed that the crystal lattice of the nickel grows insuffi-

ciently. If the nickel is completely amorphous, it should show a broad and gently sloping diffraction pattern, as can be seen for zinc hydroxide in Fig. 5–7 (d). The broad line is apt to be missed when sharp lines of other substances overlap. It will be noticeable if zinc and zinc oxide are removed from the precipitated nickel, or from U–Ni–B.

Digestion of the precipitated nickel with 20 % sodium hydroxide solution at 80° C was repeated two or three times. The diffraction of this sample (Fig. 5–8 (d)) exhibits three weak lines, which were originally the most intense ones, due to zinc oxide; lines associated with zinc are completely missing. Zinc is removed almost completely by high temperature treatment with concentrated alkali. In Fig. 5–8 (d), a diffuse band appears around 43.9°, at the expense of the zinc lines. It is supposed to correspond to the 44.58° line of nickel, but the lines expected at 51.9° and 76.5° are completely absent.

To remove zinc and zinc oxide, the precipitated nickel was warmed with 10 % acetic acid. This is the technique which was developed to prepare U–Ni–A. The diffraction patterns of the sample are shown

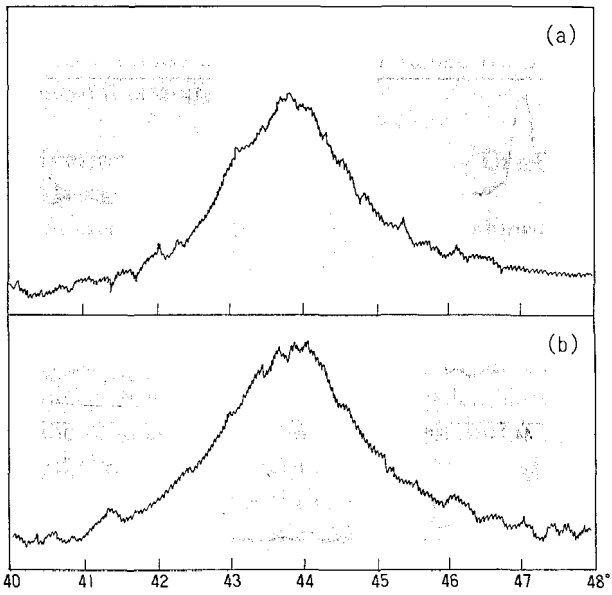


Fig. 5–9. X-ray Diffraction of U–Ni–A and U–Ni–B

(a) U–Ni–B (treated with 20% NaOH at 80°C)

(b) U–Ni–A (treated with 10% acetic acid at room temperature)

in Figs. 5–8 (e) and 5–9 (b). There are no lines corresponding to zinc and zinc oxide, showing that these contaminants are almost completely removed by the acetic acid treatment. A diffuse band still persists around 44°, and is attributed to nickel.

The diffuse diffraction pattern obtained from the Urushibara nickel catalyst is perhaps from the (111) plane of face-centered cubic nickel. It is concluded that Urushibara nickel has an insufficient lattice structure.

(d) Nickel Catalyst Obtained from Nickel Formate

Figure 5–10 (a) illustrates the diffraction pattern of a nickel catalyst, prepared by the thermal decomposition of nickel formate in paraffin, followed by treatment with petroleum ether to remove the paraffin and subsequent treatment with water and ethanol. It exhibits three diffuse lines around 44.0°, 51.1°, and 74.7°, which clearly correspond to the diffraction lines of face-centered cubic nickel. These three lines are far more diffuse than the corresponding lines of nickel obtained from nickel carbonyl (Fig. 5–6), showing that the crystal growth of nickel obtained from nickel formate is more or less insufficient.

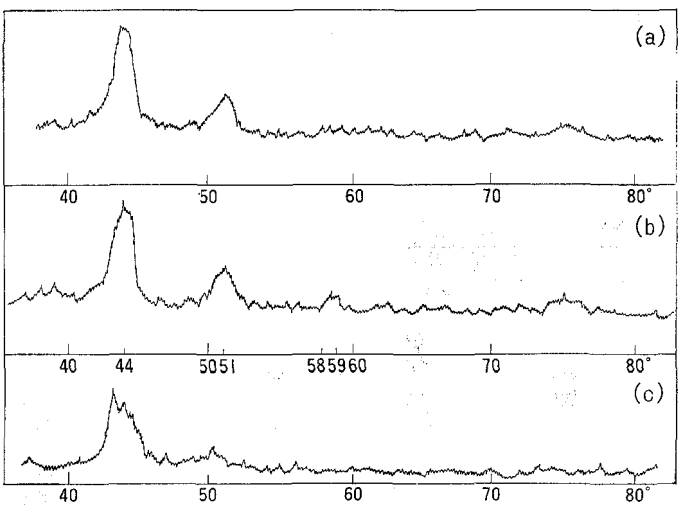


Fig. 5–10. X-ray Diffraction of Nickel Catalysts

(a) nickel catalyst from nickel formate
(b) identical to (a), after treatment with 10% NaOH
(c) Raney nickel W–2

The diffraction pattern of another sample of nickel obtained by the thermal decomposition of nickel formate, followed by treatment with 10 % sodium hydroxide solution at 55° C, is illustrated in Fig. 5–10 (b). The general aspects of this pattern are almost the same as those of the diffraction pattern of the same nickel sample before alkali treatment, but a weak and diffuse peak arises near 58.7°, showing that some reaction took place between the nickel and the alkali.

(*e*) *Raney Nickel*

The X-ray diffraction pattern of Raney nickel W–7 cannot be obtained, as it ignites upon exposure to air. The diffraction pattern of W–2 type Raney nickel is illustrated in Fig. 5–10 (c). It shows two diffuse lines around 44° and 50.3°, which seem to correspond to those characteristic of face-centered cubic nickel, but the line corresponding to the 76.5° diffraction is completely missing.

In Urushibara nickel, Raney nickel, and nickel obtained from nickel formate, the (111) diffraction at 44° is present, though diffuse. The line at 51.9° from the (200) plane is fairly well defined in nickel obtained from nickel formate, but is only barely perceptible in Raney nickel, and is completely missing in Urushibara nickel. The line at 76.5° from the (220) plane is observable only in nickel obtained from nickel formate, though even here it is quite diffused.

5. 2. 2. Activation Mechanism for Obtaining Urushibara Nickel Catalysts from Precipitated Nickel

The precipitated nickel obtained from nickel chloride solution and zinc dust has no catalytic activity by itself, but acquires activity when treated with alkalis or acids. The activation mechanism has been elucidated by X-ray diffractions studies.

The precipitated nickel consists of a large amount of zinc powder coated with nickel metal, and contains a considerable amount of contaminating zinc oxide, which comes from zinc dust. Zinc hydroxide may be present owing to the reaction between zinc and water. It may also be produced at the expense of the zinc metal, when the precipitated nickel is digested with sodium hydroxide solution. Therefore, highly active U–Ni–B, produced by this process, may still contain large amounts of zinc, zinc oxide, and zinc hydroxide, together with nickel metal, which is responsible for the catalytic activity.

Another experiment showed that chloride ions appear in solution when precipitated nickel obtained from nickel chloride, washed until

the wash water no longer contained any trace of chloride ion, was warmed with sodium hydroxide solution. This was also the case when the precipitated nickel was treated with acetic acid. Therefore, it was concluded that the precipitated nickel contained some chlorine compound insoluble in water but soluble in both alkali and acetic acid. It was assumed that the substance was zinc hydroxide chloride Zn(OH)Cl, which was confirmed as follows:

The X-ray diffraction pattern of the precipitated nickel (Fig. 5–7 (a)) shows lines associated with zinc, zinc oxide, and zinc hydroxide chloride, but those corresponding to nickel are missing. The X-ray diffraction pattern of U–Ni–B (Fig. 5–8 (a)) lacks the zinc hydroxide chloride line, although other lines remain. In the diffraction pattern of U–Ni–A (Fig. 5–8 (e)), lines associated with zinc and zinc oxide also disappear, and only a diffuse reflection, which may be attributable to the (111) plane of nickel, remains.

A comparison of these diffraction patterns clearly shows that a large amount of zinc hydroxide chloride is formed when nickel chloride solution reacts with zinc dust, covering the surface of the precipitated nickel, and that this is removed by alkali or acid treatment. The precipitated nickel acquires high activity on treatment with either alkali or acetic acid. Active U–Ni–B catalyst still contains large amounts of zinc and zinc oxide, but zinc hydroxide chloride is removed completely. Thus it is very probable that the activating effect of alkalis or acids consists in exposing the inherently active nickel surfaces of the precipitated nickel by removing zinc hydroxide chloride, and not in creating any active substances or active state on the surfaces.

The rate of dissolution of zinc hydroxide chloride by alkali is remarkable compared with that of zinc. Therefore, a comparatively small amount of alkali suffices to rapidly remove zinc hydroxide chloride, producing U–Ni–B of highest activity, with most of the zinc and zinc oxide remaining intact. On the other hand, a small amount of acid produces only low activity, and highly active U–Ni–A catalyst is produced only when the precipitated nickel is treated with an excess of acid, so that the zinc disappears completely and even part of the nickel is dissolved, making the solution greenish. The reason would appear to be that zinc hydroxide chloride is not removed completely by an amount of acid sufficient to dissolve all the zinc metal. This is consistent with the following experimental results:

Several samples of active U–Ni–B catalyst were further treated with varying amounts of acetic or propionic acid, and compared with each

Table 5–1. Activity of U–Ni–B after Additional Acid Treatment

Sample: nitrobenzene (0.02 mole, 2.46 g) in ethanol (20 ml)
Conditions: Atmospheric pressure, 25°C

Kind and volume of acid (ml)[a]	None	Propionic acid				Acetic acid		
		6	8	10	12	5	6	7
Activity (ml)[b]	265	177	283	233	212	243	286	258

[a] This is diluted with water to 80 ml to treat U–Ni–B containing 0.4–0.5 g of nickel.
[b] Amount of hydrogen uptake during the first 10 minutes.

other with respect to their catalytic activities. In Table 5–1 are listed the volumes (ml) of hydrogen absorbed during the first 10 minutes when nitrobenzene (2.46 g, 0.02 mole) in ethanol (20 ml) was reduced in the presence of these catalysts (corresponding to 0.4–0.5 g Ni). We see that an insufficient amount of acid brought about a reduction in the activity of U–Ni–B, perhaps owing to the formation of zinc hydroxide acetate or propionate, which tends to cover the active surfaces of the

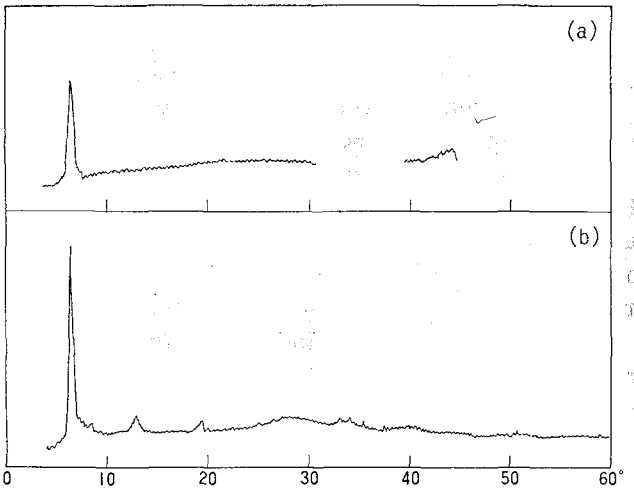


Fig. 5–11. X-ray Diffraction of Zinc Hydroxide Acetate and Precipitated Nickel Treated with an Insufficient Amount of Acetic Acid

(a) U–Ni–A prepared by treating the precipitated nickel with an insufficient amount of acetic acid
(b) zinc hydroxide acetate

nickel. This assumption also conforms to the X-ray diffraction studies. Precipitated nickel obtained from nickel chloride solution (containing 0.5 g of nickel) and 5 g of zinc dust was treated with an insufficient amount of acetic acid (6 ml of acetic acid in 74 ml of water). The catalyst thus obtained proved to have an activity less than half that of ordinary U–Ni–A (cf. Chapter 4, Table 4–2), and its diffraction pattern exhibits a sharp line at 6.6° (2θ) (Fig. 5–11(a)). The X-ray diffraction of zinc hydroxide acetate, prepared by the addition of sodium hydroxide to a mixture of zinc dust and dilute acetic acid until the solution was neutral to phenolphthalein, also shows the same distinct 6.6° line (Fig. 5–11 (b)). Therefore, it was confirmed that insufficient acid produces zinc hydroxide acetate in U–Ni–A catalyst.

As we shall see in section 6. 4. 2(*c*), spent U–Ni–A or U–Ni–B, once exposed to air and deactivated, can be regenerated by the addition of zinc dust and an excess of acetic acid. They then acquire activities comparable to newly prepared U–Ni–A catalyst.[36] Sodium hydroxide in place of acetic acid gives poorer results. It is suggested that treatment with acetic acid not only liberates hydrogen and removes poisoning substances (zinc hydroxide chloride, etc.), but erodes the surfaces of the nickel particles, and creates new active surfaces. It is also known[36] that the activity is almost the same as that displayed by ordinary U–Ni–A or U–Ni–B, when precipitated nickel obtained from nickel chloride solution and zinc dust is dried at about 100° C and stored for a week in the air, and then treated with sodium hydroxide solution or aqueous acetic acid. Therefore, further investigation is required to establish whether precipitated nickel has inherently active nickel surfaces or not. At any rate, the nickel metal in precipitated nickel, no doubt, already has some intrinsic structure which accounts for its catalytic activity (see the following section). Readers are already familiar with activation by removing zinc hydroxide chloride with alkali or acid.

5. 2. 3. Crystallite Size and Catalytic Activity

Conditions under which the best U–Ni catalyst can be prepared have been examined in detail. Water, ethanol, and ethylene glycol were used as solvents for preparing precipitated nickel from nickel chloride solution and zinc dust, and either the concentration of the nickel chloride or the reaction temperature was varied. The precipitated nickel was digested with sodium hydroxide solution or acetic acid, under varied concentrations and digestion temperatures. The

catalytic activities of the products were determined by the rate of absorption of hydrogen by nitrobenzene in their presence.

X-ray diffractions of the products were also observed and their crystallite sizes were calculated from the line widths. They were compared with the results of catalytic reductions, and a relation between crystallite size and catalytic activity was established.

Alexander and Klug*1) examined in detail a method of obtaining crystallite size from the width of the X-ray diffraction lines, and calculated the crystallite sizes of several nickel catalysts. For example, the dimension perpendicular to the (111) plane of Raney nickel was estimated to be 43 Å. Their method is as follows:

The fluctuating profile of the X-ray diffraction pattern is smoothed out by plotting the mid-points of the fine zig-zag curves, as is shown in Fig. 5–12, and the half-width B_0 is obtained as the distance between points on the smooth curve at half-maximum intensity.

The corresponding half-width b_0 for the macro quartz crystals, in which no broadening of the diffraction lines is observed, is taken as the natural width for obtaining the pure diffraction breadth β. B_0 and b_0 are calibrated*2) by taking into account the overlapping of the peaks due to the doublet $K_{\alpha 1}$ and $K_{\alpha 2}$ of copper. The calibrated values are referred to as B and b, respectively. B_0 does not need to be corrected, if it is large. The crystallite size is calculated by Scherrer's formula:

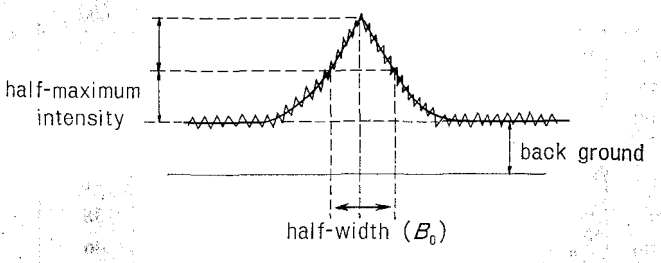


Fig. 5–12. Evaluation of Half-width

*1) L. Alexander and H. P. Klug, *J. Appl. Phys.*, **21**, 126, 137 (1950): H. P. Klug and L. Alexander, "X-ray Diffraction Procedure," John Wiley & Sons, N. Y. (1951).

*2) F. W. Jones, *Proc. Roy. Soc.*, A, **116**, 16 (1938).

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta}$$

where, D_{hkl}=mean thickness of crystallite perpendicular to the (*hkl*) plane;
K=shape factor (estimated from the literature to be 0.9[*1]);
λ=wavelength of applied X-rays (1.54 Å for Cu–K_α);
θ=glancing angle;
β=pure diffraction width (in radians).

$$\beta^2 = B^2 - b^2$$

The value β may conveniently be replaced by B_0, when the latter is as large as about 2°. B. E. Warren[*2] found that the correction with b_0 is unnecessary when $b_0 < B_0/5$. The β_0 value, 0.18°, of quartz powder (about 10 μ in dimension) is used for evaluating β of Urushibara nickel catalyst. As b_0 is smaller than $B_0/10$ in this case, we may safely replace β by B_0, confining the error in D to within 1 Å.

The dimension of the crystallites of Urushibara nickel catalysts may thus be estimated by means of the modified Scherrer's formula:

$$D = \frac{0.9\lambda}{B_0 \cos\theta}$$

Table 5–2. Aspects of Diffractions of Various U–Ni–B Catalysts

Concentration of $NiCl_2 \cdot 6H_2O$ (g/ml)	Solvent	Temperature of reaction with zinc dust (°C)	Temperature of reaction with 20% NaOH (°C)	Dimension of (111) plane (Å)	Position of (111) peak (2θ)
2 g/10 ml	water	100	80	41	43.9°
„	„	room temp.	80	48	44.1°
2 g/100 ml	„	100	80	52	44.0°
„	„	room temp.	80	59	44.1°
2 g/10 ml	„	100	room temp.	41	44°
2 g/10 ml	ethanol	80	80	38	43.85°
2 g/100 ml	„	80	80	46	44°
„	„	room temp.	80	61	44.3°
2 g/10 ml	ethylene glycol	120	80	43	43.9°
„	„	room temp.	80	42	43.9°

*1) L. Alexander and H. P. Klug, *J. Appl. Phys.*, **21**, 126, 137 (1950).
*2) B. E. Warren, *J. Appl. Phys.*, **12**, 375 (1941).

Table 5–3. Aspects of Diffractions of Various U–Ni–A Catalysts

Concentration of $NiCl_2 \cdot 6H_2O$ (g/ml)	Solvent	Temperature of reaction with zinc dust (°C)	Conditions of the reaction with acetic acid	Dimension of (111) plane (Å)	Position of (111) peak (2θ)
2 g/10 ml	water	100	10% AcOH, room temp.	37	43.8°
"	"	100	10% AcOH, room temp.; then 30% AcOH, cooling	44	43.9°
"	"	100	20% AcOH, 55°C	49.5	44°
"	ethylene glycol	160	12.5% AcOH, room temp.	41	44°

Values for the crystallite size of Urushibara nickel catalysts prepared under various conditions are given in Table 5–2 and 5–3. For the sake of comparison, the crystallite sizes of Raney nickel, nickel obtained from nickel carbonyl, and other nickel catalysts are tabulated in Table 5–4.

The catalytic activities of Urushibara nickel catalysts prepared under various conditions are estimated in the following way:

Samples of precipitated nickel, prepared under different conditions

Table 5–4. Aspects of X-ray Diffraction of Various Nickel Catalysts

Catalyst	Treatment	Dimension of (111) plane (Å)	Position of (111) peak (2θ)
nickel from nickel formate	thermal decomposition in paraffin	52	44°
"	treatment of above sample with 10% NaOH at a high temperature	50	43.9°
"	thermal decomposition at a lower temperature	92	44.4°
Raney nickel		43[a]	~44°
nickel from nickel carbonyl[b]	thermal decomposition	ca. 600	44.58°
nickel from nickel oxide	reduction with hydrogen at 330°C	ca. 350	44.54°
"	reduction with hydrogen at 400°C	ca. 380	44.58°

[a] L. Alexander and H. P. Klug, *J. Appl. Phys.*, **21**, 126 (1950).

[b] Useless as a hydrogenating catalyst.

Table 5–5. Relation between the Activity of U–Ni–A and Its Crystallite Size

Catalyst: U–Ni–A containing ca. 0.5 g of nickel
Sample: $2/3\times10^{-2}$ mole of nitrobenzene (0.82 g) in ethanol (20 ml)
Conditions: Atmospheric pressure, 25—26°C

No.	Conditions of the preparation of precipitated nickel		Conditions of acid treatment			Activity (ml/min)	Dimension of (111) plane (Å)
	Concentration of $NiCl_2$ solution (g-Ni/ml)	Temprature of the reaction with zinc dust (°C)	Acid	Concentration of acid (%)	Total volume (ml)		
1	0.5 g/50 ml	room temp. —100	acetic acid	13	80	19	59
2	0.5 g/5 ml	room temp.	„	„	„	25	45
3	0.5 g/50 ml	100	„	„	„	25	44
4	0.5 g/5 ml	100	„	„	„	29	41
5	0.5 g/5 ml	100	propionic acid	20	„	34	37

from zinc dust and nickel chloride solution (corresponding to 0.5 g of nickel), were treated with acetic acid or propionic acid. In the presence of each of these U–Ni–A catalysts, nitrobenzene was reduced at room temperature and under ordinary pressure in ethanol. The volume of hydrogen absorbed per minute was obtained from an average over the first 4 or 5 minutes, and regarded as a measure of catalytic activity (Table 5–5).

From the comparison between crystallite size and catalytic activity, the following conclusions were reached:

(1) The crystallite size of Urushibara nickel catalyst tends to become smaller as the reaction between the nickel chloride solution and zinc dust becomes more violent.

(2) The crystallite size of Urushibara catalyst is almost the same, irrespective of whether sodium hydroxide or acetic acid is used to digest the precipitated nickel. The temperature of digestion also has little effect. Crystallite size is mainly determined by the conditions under which the precipitated nickel is produced, and precipitated nickel prepared under the same conditions gives U–Ni–A or U–Ni–B catalysts of similar crystallite size.

(3) The catalytic activity falls as crystallite size increases (Fig. 5–13). Assuming every crystallite to be a cube or of similar form, the

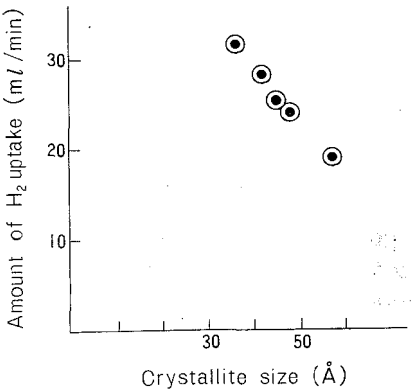


Fig. 5–13. Relation between Crystallite Size and Catalytic Activity

total surface area of a definite weight of nickel should be inversely proportional to the size of the crystallite. Assuming again that the catalytic activity is proportional to the surface area of the catalyst, in this narrow range the product of activity and crystallite size should be constant. This conclusion agrees well with Fig. 5–13, in which the curve may be regarded as part of a parabola.

(4) The ion-exchange reaction takes place as well in ethanol or ethylene glycol, in place of water. The precipitated nickel obtained is digested as usual with sodium hydroxide or acetic acid, giving Urushibara nickel catalysts. The crystallite size is similarly decided by the conditions of the ion-exchange reaction. When the crystallite size of the catalyst is as low as about 40 Å, the catalyst exhibits high activity, and can be used for catalytic reduction (Tables 5–2 and 5–3).

(5) The crystallite size of Urushibara nickel is almost the same as that of Raney nickel, which is estimated to be 43 Å (Table 5–4 and note). Many experiments have confirmed that the activity of Urushibara catalyst is almost the same as that of Raney nickel.

(6) The crystallite size of nickel obtained from nickel formate depends on the temperature at which the nickel formate is decomposed. It is always larger than the crystallite size of Urushibara nickel, and the catalytic activity is lower.

(7) The crystallite size of nickel prepared by the thermal decomposition of nickel carbonyl, or of reduced nickel prepared by the reduction of nickel oxide with hydrogen, is always very large. These specimens

show no activity in the reduction of nitrobenzene at ordinary temperature and pressure.

We see that the activity of nickel catalysts is a function of the crystallite size and increases with decreasing size. As acid or base treatment at the stage of activation has little effect on the crystallite size of the precipitated nickel, the conditions under which precipitated nickel is prepared determine the crystallite size and the maximum activity of the catalyst. The possibility of obtaining a catalyst of increased activity, therefore, is solely dependent on whether the optimum conditions for reducing the crystallite size can be reached.

5. 2. 4. Fall-off of Activity and Crystallite Size

The activity of Urushibara nickel catalyst falls off rapidly when it is stored in water or ethanol. It is readily deactivated when dried in air. However, the crystallite size does not change appreciably in any of such deactivated catalysts; *e.g.*, in catalysts stored in ethanol for 3 months at room temperature, catalysts dried in a desiccator for 3 months, or catalysts heated with an alkali solution at 100° C. This is also true for spent catalysts, used once in the reduction of nitrobenzene. It seems that fall-off or loss of activity is accompanied by no change in crystal structure, as indicated by X-ray diffraction. This subject needs to be investigated from other points of view.

5. 3. X-ray Diffraction Studies, Part II[39]

We have seen thus far that X-ray diffraction technique has succeeded in establishing the activation mechanism of Urushibara nickel by acid or alkali treatment and that the activity of nickel catalysts was found to be a function of crystallite size. This success was followed by a great number of further experiments, which dealt with the catalytic activity of Urushibara nickel and Urushibara iron as related to crystal structure, again with the aid of X-ray diffraction. It is recalled that the Urushibara iron catalysts U–Fe(II) and U–Fe(III) have unique activity toward partial hydrogenation of acetylenic compounds, whereas U–Fe–BA is entirely inactive. In what follows we shall discuss some interesting results which have led to an understanding of the nature of the activity of Urushibara catalysts.

5. 3. 1. X-ray Diffraction Patterns of Urushibara Nickel Catalysts

As was seen in a foregoing section, U–Ni–B contains large amounts

Table 5–6. X-ray Diffractions of Various U–Ni–A Catalysts

Concentration of nickel[a]: 1 g/14 ml
Temperature of the exchange reaction: 100°C

No.[b]	Sample	Digesting agent	B_0 (°)	Position of peak (2θ) (°)	Dimension of crystallite (Å)
1[c]	U-Ni-A	13% AcOH	1.5	44.4	57.4
2[c]	U-Ni-A	„	1.6	44.4	53.9
3[c]	U-Ni-A(HCl)	0.75 N HCl	2.0	44.0	43.1
4	U-Ni-A	13% AcOH	2.4	43.8	35.5
4	U-Ni-A	„	2.2	43.8	38.7
4	U-Ni-A(HCl)	0.75 N HCl	2.4	43.6	35.5
5	U-Ni-A	13% AcOH	2.1	43.9	40.8
5	U-Ni-A	„	2.1	43.9	40.8
5	U-Ni-A(HCl)	1.5 N HCl	1.7	43.9	50.4
6	U-Ni-A	13% AcOH	2.0	43.9	42.8
7	U-Ni-A	„	2.1	43.7	40.7
7	U-Ni-A	20% AcOH	2.2	43.7	38.9
8	U-Ni-A	„	2.1	43.6	40.6
9	U-Ni-A	„	2.1	43.6	40.6
10	U-Ni-A	„	2.3	44.0	37.2

[a] 1 g of nickel corresponds to 4.04 g of nickel chloride crystals, $NiCl_2 \cdot 6H_2O$.
[b] Different catalysts with the same number were prepared from the same precipitated nickel.
[c] Samples left standing for about 4 years.

of zinc and zinc oxide, and its X-ray diffraction pattern shows lines associated with these contaminants; however lines associated with nickel are not clearly observed (Fig. 5–8 (a)). On the other hand, U–Ni–A contains comparatively small amounts of these contaminants and its diffraction pattern shows a diffuse profile with a peak near 44°, which may be ascribed to the (111) plane of nickel (Fig. 5–8 (e) and 5–9 (b)). In Tables 5–6 through 5–8 are tabulated detailed data on many U–Ni–A, U–Ni–BA, and U–Ni–AA catalysts, from which we can see at once several interesting points.

First, the crystallite sizes of U–Ni–A(s) catalysts are in general smaller than those of U–Ni–A catalysts. This fact seems to contradict the smaller activity of U–Ni–A(s).[37]

The apparent catalytic activity for reduction at high pressure may be governed practically by several factors: (1) the sufficient presence

Table 5–7. X-ray Diffractions of U–Ni–A Catalysts

No.	Sample	Concentration of nickel[a] (g/ml)	Temperature of the exchange reaction (°C)	Digesting agent	B_0 (°)	Position of peak (2θ) (°)	Dimension of crystallite (Å)
1	U-Ni-A(s)	1 g/6 ml	room temp. —ca. 60[c]	13% AcOH	2.2	44.0	39.0
2	U-Ni-A(s)(HCl)	1 g/6 ml	room temp. —ca. 60[c]	1 N HCl	2.0	43.8	42.6
3	U-Ni-A(s)	1 g/6 ml	room temp. —ca. 60[c]	20% AcOH	2.3	44.1	37.2
4	U-Ni-A(s)	1 g/6 ml	room temp. —ca. 60[c]	„	2.1	44.1	40.8
5	U-Ni-A(s)	1 g/6 ml	room temp. —ca. 60[c]	„	2.2	44.0	39.0
6	U-Ni-A(s)	1 g/6 ml	room temp. —ca. 60[c]	„	2.3	44.0	37.2
7	U-Ni-A[b]	1 g/31 ml	100	13% AcOH	2.2	43.9	38.9
8	U-Ni-A[b]	1 g/31 ml	100	„	1.8	43.3	47.4
9	U-Ni-A[b]	1 g/31 ml	100	„	2.0	43.4	42.6
10	U-Ni-A[b]	1 g/31 ml	100	„	2.0	44.0	43.1
11	U-Ni-A[b]	1 g/31 ml	100	„	2.0	43.9	42.8
12	U-Ni-CA	1 g/14 ml	room temp.	10% AcOH	1.9	43.7	45.0
13	U-Ni-CA	1 g/14 ml	room temp.	„	2.1	43.9	40.8
14	U-Ni-CA	1 g/14 ml	room temp.	13% AcOH	2.0	43.8	42.6
15	U-Ni-CA	1 g/14 ml	room temp.	„	2.0	44.0	43.1

[a] 1 g of nickel corresponds to 4.04 g of nickel chloride crystals, $NiCl_2 \cdot 6H_2O$ or 4.24 g of nickel acetate $Ni(CH_3CO_2)_2 \cdot 4H_2O$.

[b] Prepared from nickel acetate, instead of nickel chloride.

[c] Temperature rises spontaneously to 60°C on account of the heat of reaction.

Table 5–8. X-ray Diffractions of U–Ni–BA and U–Ni–AA

Concentration of nickel: 1 g/15 ml

No.	Sample	Temperature of the exchange reaction (°C)	Digesting agent	B_0 (°)	Position of peaks (2θ) (°)		D_{111} (Å)
					(111)	(200)	
1	U–Ni–BA	50–70	20% NaOH	0.6	44.6	51.9	143.6
2	U–Ni–BA	50–70	„	0.6	44.6	52.0	143.6
3	U–Ni–BA	50–70	„	0.8	44.5	51.8	107.8
4	U–Ni–BA	50–70	„	0.5	44.6	51.9	172.3
5	U–Ni–BA	50–70	„	0.9	44.5	51.8	95.7
6	U–Ni–BA	room temp.	„	0.7	44.59	51.9	123.1
7	U–Ni–AA	50–70	40% AcOH NaCl	0.7	44.4	51.7	123.2

of an appropriate texture in the metal particles; (2) the weight of the catalyst; (3) the apparent size of the catalyst grains; (4) the dispersability of the catalyst into solution (this factor may be decided either by the size of the catalyst grains or by the amount of contaminating substances; it is recalled that U–Ni–B catalysts contain large amounts

Table 5–9. Aspects of Nickel (f.c.c.), α–Iron (b.c.c.), and Zinc (h.c.p.), as revealed by X-ray Diffraction

	(*hkl*)	Interplanar spacing *d* (Å)	Diffraction angle[a] 2θ (°)	Intensity
Ni	(111)	2.03	44.58 (Cu)	1.00
	(200)	1.76	51.90 (Cu)	0.50
	(220)	1.244	76.50 (Cu)	0.32
	(311)	1.061	88.05 (Cu)	0.32
α–Fe	(110)	2.0268	57.10 (Fe)	1.00
	(200)	1.4332	85.0 (Fe)	0.19
	(211)	1.1702	111.7 (Fe)	0.30
Zn	(101)	2.094	43.3 (Cu) 55.2 (Fe)	1.00
	(002)	2.473	36.3 (Cu) 46.1 (Fe)	0.53
	(100)	2.308	39.1 (Cu) 49.7 (Fe)	0.40

[a] Cu–K_α or Fe–K_α

of zinc and zinc oxide); (5) the reaction temperature; (6) the pressure of hydrogen; (7) the kind and volume of solvent; (8) the efficiency of stirring or shaking; and (9) the kind and purity of material to be reduced.

Of these factors, the first would account for the lower activity of U–Ni–A(s), because the weight of U–Ni–A(s) relative to that of a definite amount of nickel is somewhat smaller than that of U–Ni–A. Factors (5) through (9) have to do only with experimental conditions and (3) and (4) can be assumed not to vary greatly.

Second, a curious difference is seen between the diffraction pattern of U–Ni–A and that of U–Ni–BA or U–Ni–AA. Both U–Ni–BA and U–Ni–AA exhibit peaks from the (111) and (200) planes of nickel at the correct positions (Fig. 5–14, cf. Table 5–9). In contrast, the diffraction of U–Ni–A shows only a diffuse profile; the estimated peak position of the (111) plane of nickel seems to shift towards a lower angle from

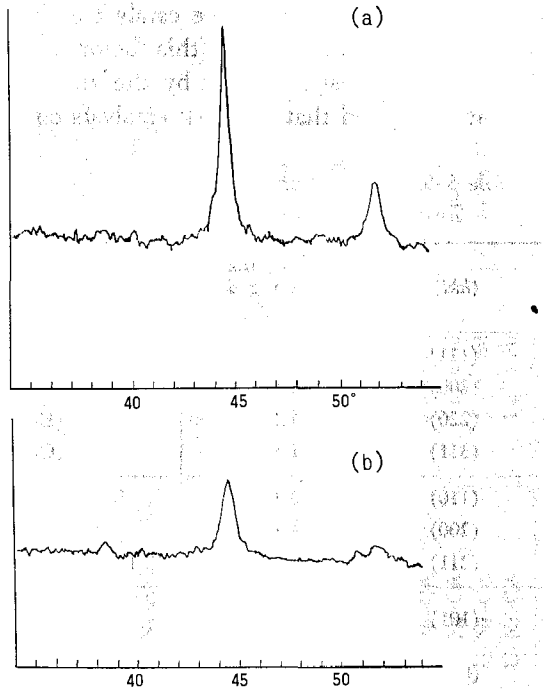


Fig. 5–14. X-ray Diffraction Diagrams of U–Ni–BA and U–Ni–AA

(a) U–Ni–BA; (b) U–Ni–AA

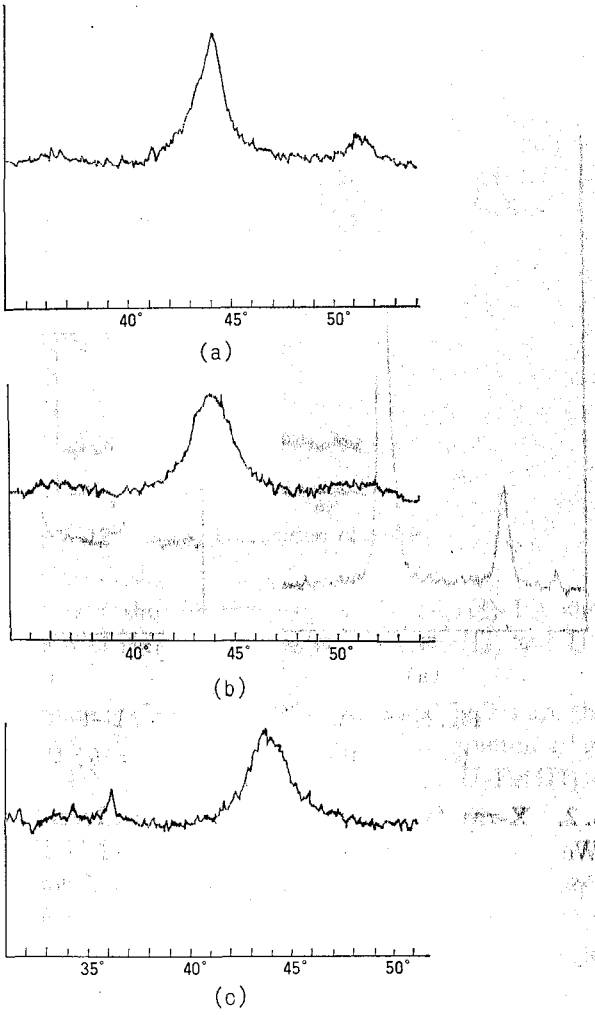


Fig. 5–15. X-ray Diffraction of Various U–Ni–A Catalysts
(a) U–Ni–A; (b) U–Ni–A(s); (c) U–Ni–A (from nickel acetate)

the correct position (Fig. 5–15). It is well known that for a crystal composed of tiny crystallites or for a crystal with disorders or dislocations, the diffraction peaks become broad, but only at the correct Bragg angles. Therefore, it is very likely that the lattice is somewhat modified in U–Ni–A catalysts. This is also the case for U–Ni–B, as can be verified from Table 5–2.

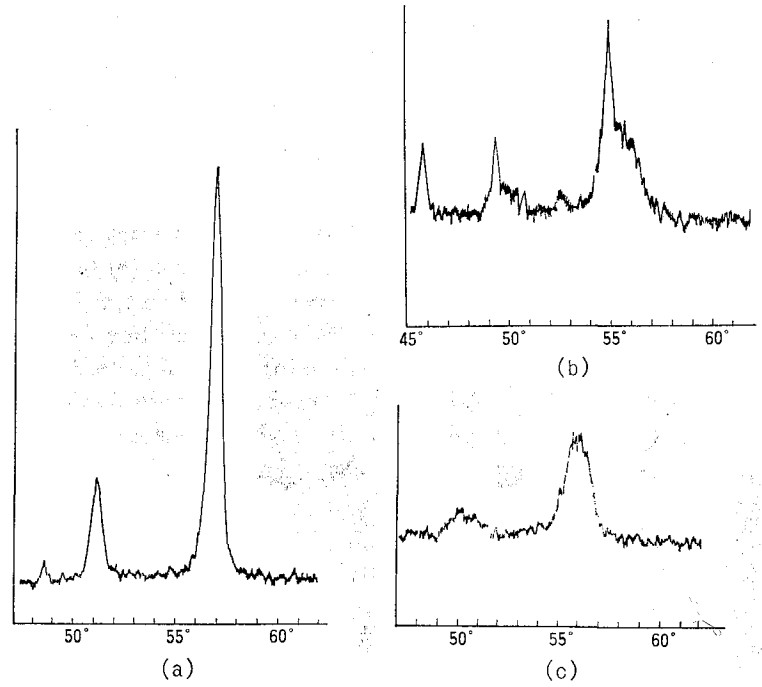


Fig. 5–16. X-ray Diffraction of U–Fe Catalysts
(a) U–Fe(III)–BA; (b) U–Fe(II); (c) U–Fe(III)

5. 3. 2. X-ray Diffraction of Urushibara Iron Catalysts

We have already found that U–Fe(II) and U–Fe(III) are active for the partial hydrogenation of 2-butyne-1,4-diol, and give 2-butene-1,4-diol, whereas U–Fe(III)–BA is entirely inactive.[38] The former two catalysts are prepared by acetic acid treatment of precipitated iron, which is obtained from zinc dust and iron(II) or iron(III) chloride, respectively. The latter catalyst is obtained by alkali treatment of precipitated iron which is obtained from aluminum and iron(III) chloride.

The X-ray diffraction patterns of these catalysts are shown in Fig 5–16. The diffraction of U–Fe(III)–BA with an Fe–K_α beam shows the regular (110) plane lines of α-iron (see Fig. 5–17 and Table 5–9), with a minor shift towards lower angles (0.3°), the glancing angle 2θ being 56.8°. In contrast, U–Fe(II) and U–Fe(III) exhibit diffuse lines with peaks far removed from the correct position, the peak positions of the two catalysts being estimated to be 55.7° and 55.3° respectively.

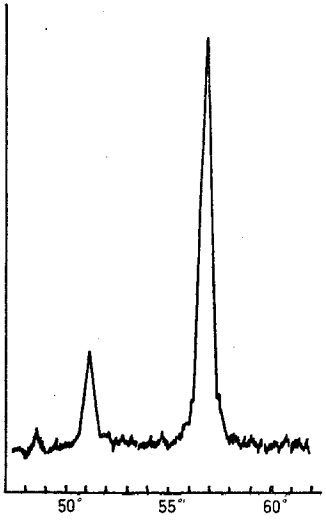


Fig. 5–17. X-ray Diffraction of α–Fe

We again confirm that the inactive catalyst U–Fe(III)–BA shows the ordinary diffraction of α-iron, whereas active U–Fe(II) and U–Fe (III) do not.

Other sharp peaks in Fig. 5–16(b) (45.8°, 49.4°, and 54.9°) are those of zinc (see Table 5–9). We see at once that a large amount of zinc is contained in U–Fe(II), but only a trace, if any, in U–Fe(III) and U–Fe(III)–BA.

5. 3. 3. Origin of Activity of the Urushibara Nickel Catalysts

The origin of activity of the Urushibara catalyst is anything but definitely established. However, S. Taira has suggested what may bring about the activity of Urushibara catalysts.[39]

The crystal structures of U–Ni–A and U–Ni–B seem to be very different from that of U–Ni–BA; and also, the structures of U–Fe(II) and U–Fe(III) from that of U–Fe(III)–BA. Comparing their activities in hydrogenation, it is found, as noted previously, that a substantial difference in activity exists parallel to the structural difference. Therefore, the activity of the Urushibara catalysts should be traced back to their crystal structure.

We are already familiar with the fact that the preparation of the Urushibara catalysts consists of two steps—the production of precipitated metal, and digestion with acid or alkali. This might remind the

reader of Raney catalyst being produced from Raney alloy. The resemblance, however, is accidental and the precipitated nickel is essentially different from Raney alloy. With Raney nickel, crystallization of the nickel would take place when aluminum is dissolved by alkali from Raney alloy, as this is a homogeneous mixture of nickel and aluminum. In the case of Urushibara nickel catalyst, on the other hand, crystallization is already complete when the precipitated nickel is produced, as the nickel metal deposits on the surface of zinc or aluminum. Digestion only serves to remove substrate zinc or aluminum metal and their compounds. Therefore, the grains of both catalysts should be different, although their activities are very similar. The activity of Urushibara nickel catalyst is a function of the reaction conditions under which the precipitated nickel is prepared, and is little affected by the conditions under which it is digested.[13]

To fully explain the very different diffraction patterns of U–Ni–A and U–Ni–BA, the methods of preparing the precipitated nickel must be considered in detail. The precipitation of nickel metal on another metal surface closely resembles the formation of an evaporated film. Electron diffraction has revealed that epitaxy, *i.e.*, oriented overgrowth, occurs in an evaporated film.*[1] There is a correlation between the orientation of the deposited crystallites and that of the substrate crystals, although the structure of the crystallite is usually the same as would be found in macro crystals. However, Schulz*[2] has observed that many substances which usually have a cesium chloride structure happened to crystallize with a sodium chloride structure when they were evaporated on lithium fluoride, sodium chloride, potassium bromide, or mica, on which such oriented overgrowth frequently takes place.

Such would also be the case for the precipitated nickel. Nickel, which usually has a face-centerd cubic structure (f.c.c.) may take a hexagonal closest packed structure (h.c.p.) as a modification. It is suggested that nickel precipitated on zinc is forced to crystallize in a h.c.p. structure, as the substrate zinc metal has this structure. As epitaxial growth is very often accompanied by lattice defects, the diffraction patterns of U–Ni–A and U–Ni–B are understood to involve crystallite structure with many lattice deformations. The diffractions exhibit diffuse peaks, which split into several fine peaks, and their apparent maxima shift toward higher angles than would be expected

*1) D. W. Pashley, *Advances in Physics*, **5**, 173 (1956).
*2) L. G. Schulz, *Acta Cryst.*, **4**, 487 (1951).

for an ideal h.c.p. structure. If the catalysts have a true h.c.p. structure, the diffractions would exhibit sharp peaks and their positions would be very close to those of zinc. Therefore, the shift can be considered as a measure of the extent that the crystal is deformed from an h.c.p. to an f.c.c. structure. The f.c.c. structure is a stable phase, free from any large defect; the shift may also be regarded as an inverse measure of the extent of defects present in Urushibara nickel catalysts. The lattice defects may offer to foreign atoms or molecules, say H or H_2, proper seats and spaces, in which they can move to a considerable extent rather than being tightly bound. Such places may be the active centers of a catalyst. Hence, apart from crystallite size, the more lattice defects that are present in a catalyst, the more likely it is to be active.

The situation is best illustrated when we compare U–Ni–A, U–Ni–A(s), and U–Ni–CA with each other, or when we compare U–Ni–A catalysts prepared from different nickel salts (see Table 5–6 and 5–7). The activity decreases parallel to the shift of the diffraction angle.

The diffraction of U–Ni–BA shows peaks at the regular angles for f.c.c. nickel. It is worth nothing that the aluminum on which the nickel crystals grow has an f.c.c. structure. The activity of U–Ni–BA should be of a different type.

The same thing would happen in Urushibara iron catalysts. While iron has several allotropic modifications,

$$\underset{\text{(b.c.c.)}}{\alpha\text{–Fe}} \overset{910^\circ\text{C}}{\rightleftarrows} \underset{\text{(f.c.c.)}}{\gamma\text{–Fe}} \overset{1400^\circ\text{C}}{\rightleftarrows} \underset{\text{(b.c.c.)}}{\delta\text{–Fe}}$$

the low-temperature modification (α–Fe) has a body-centered cubic structure (b.c.c.). U–Fe(III)–BA, which is prepared from iron precipitated on aluminum, shows the diffraction pattern of α–Fe, and hence must be b.c.c. This does not contradict the above discussion because the (110) plane of a b.c.c. lattice simulates the (100) plane of an f.c.c. lattice, and because the lattice dimension of aluminum is very close to the diagonal dimension of the α–iron lattice. Such a phenomenon is often encountered in epitaxial growth. For example, it is reported that NaCl type (f.c.c.) crystals often grow on a CsCl type (b.c.c.) substrate.

In U–Fe(II) and U–Fe(III), whose diffractions show unusual lines, the iron crystallizes on zinc, which has an h.c.p. structure. The epitaxial coherency relation demands that the iron crystals be h.c.p.

Owing to the unusual strain experienced by the lattice, the crystals would grow at the expense of lattice perfection, and the catalyst would become active.

The temperature of the ion-exchange reaction and the concentration of the solution may have some influence upon the crystal structure of nickel in the Urushibara catalyst, if oriented overgrowth takes place when precipitated nickel is formed. Tables 5–6 and 5–7 suggest that the lower the concentration of nickel ion in solution, the more likely the precipitated nickel is to have a structure favorable to high activity. However, another experiment[13] has shown that the more vigorous the ion-exchange reaction, the smaller the crystallite size becomes, and the more likely the catalyst is to have a high activity.

Agents used in digesting the precipitated nickel may also affect the activity of the catalyst produced, as a particular face of a metal crystal is often attacked preferentially by acid or alkali.

These secondary influences will be the subjects of future investigations.

5. 4. Electron Diffraction Studies

Electron diffraction studies of Urushibara catalysts have been carried out. The results are in good agreement with those of X-ray diffraction.

(*a*) *U–Ni–A*

S. Yamaguchi *et al.*,[10] have observed an electron diffraction from U–Ni–A. The specimen was prepared according to Preparation 4 of Chapter 4, and washed with ethanol. Two kinds of electrons, hard and soft, were used to investigate the surface of catalyst particles. The hard electrons (about 0.02 Å) can penetrate a thick layer of a particle (about 5000 Å), whereas the soft electrons (about 0.05 Å) only graze the surface of a particle. With hard electrons, the specimen exhibited the diffraction rings of nickel, zinc, and zinc oxide; those of the nickel were quite diffuse, whereas those of zinc and zinc oxide were comparatively sharp (Fig. 5–18). A similar result was obtained from X-ray diffraction of the same specimen (see Section 5. 2. 1. (*c*)), and it is very likely that the nickel in the Urushibara catalyst forms an assembly of very fine crystallites.

In a diffraction pattern of the same specimen with soft electrons (0.0490 Å), the rings from nickel are more diffuse than would be

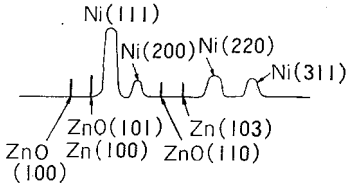


Fig. 5–18. Electron Diffraction Diagram of U–Ni–A (Wavelength 0.0284 Å)

expected from the wavelength of the electrons applied. This would imply that the surface of the nickel particles is almost amorphous.

The Urushibara catalyst is composed of nickel, zinc, and zinc oxide: zinc acts as a carrier. It is pointed out that it is not only a catalyst carrier, but protects nickel from oxidation by forming a local cell, the active centers of the nickel metal being left intact. This is also the case with Raney nickel in which aluminum plays the role of zinc in the Urushibara nickel catalyst.

(*b*) *U–Ni–BA*

I. Motoyama has observed the electron diffraction of several U–Ni–BA catalysts. The specimens were prepared according to Preparation 16 of Chapter 4, and dried under reduced pressure. A typical diffraction pattern for about 0.03 Å electrons is shown in Fig. 5–19, although the diffractions differ from each other to some extent, according to the individual samples employed.

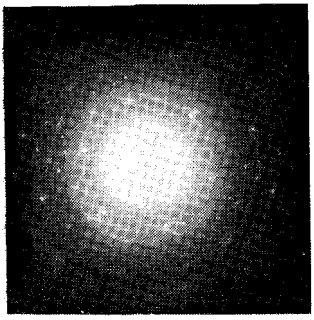


Fig. 5–19. Electron Diffraction Pattern of U–Ni–BA (Wavelength ca. 0.03 Å)

U–Ni–BA exhibits far more diffraction lines than U–Ni–A. Moreover, the lines due to nickel can be observed quite distinctly, together with those which seemingly correspond to aluminum metal, which remains after alkali treatment. This would imply that, in U–Ni–BA, the nickel crystallizes to a considerable extent. The result is consistent with that of X-ray diffraction, which shows two sharp peaks due to nickel, giving an indication of the crystallite size in U–Ni–BA (140–150 Å) (perpendicular to the (111) plane), being larger than that of U–Ni–A (40–45 Å).

5. 5. Preservation of Catalytic Activity

In general, a hydrogenating catalyst must be treated in a hydrogen atmosphere or in an appropriate solvent, avoiding even brief contact with air. A highly active catalyst will ignite if exposed to the air. U–Ni–A also happens to ignite if it is dried in air. U–Ni–B does not ignite by itself, but is readily deactivated when dried in air. The Urushibara catalysts, as well as other nickel catalysts, may preserve their activities for any desired period if they are carefully stored in a hydrogen atmosphere with the complete exclusion of air. Practically, the method is very cumbersome, and nickel catalysts for hydrogenation should be prepared each time they are required.

However, preparation of the earlier hydrogenating catalysts was both troublesome and time-consuming. One might think this is not the case with Raney catalysts, because a large amount of Raney alloy, prepared in advance or available commercially, can be stored for any length of time, from which the desired amount may be allotted for each requirement. Nevertheless, to produce a Raney catalyst, the Raney alloy must be treated with an alkali and the process, in fact, is very troublesome and time-consuming. In contrast, Urushibara catalysts can be prepared very easily. Catalysts such as U–Ni–A and U–Ni–B, are prepared from nickel chloride and zinc dust by a simple operation in only an hour or less. Preparation of U–Ni–BA from nickel chloride and aluminum grains requires a somewhat longer time than is required for the preparation of other Urushibara nickel catalysts.

As we have already seen, there is a close resemblance between Raney catalyst and Urushibara catalyst, and the analogy has, in fact, led to a speedy preparation for U–Ni–BA.[31] The method consists essentially of preparing the U–Ni–BA catalyst from precipitated nickel which is produced in advance and stored. One might think that long standing

would deactivate the finished catalyst, since the active nickel surfaces inherently present in the precipitated nickel would be impaired.

The activities of catalysts prepared in this way have been examined in the hydrogenation of phenol. The precipitated nickel was left standing for from one day to three months, either in distilled water, in 99 % ethanol, or in a dry state. Each precipitate was then treated with 20 % aqueous sodium hydroxide solution to prepare the catalyst. The activities of the individual catalysts, together with that of freshly prepared U–Ni–BA, are summarized in Table 5–10. In every case, three moles of hydrogen are absorbed and the yield of cyclohexanol was almost the same, although the time required for complete hydrogenation is somewhat longer for catalysts obtained from stored precipitated nickel. The activity of a catalyst is thus preserved, even if the precipitated nickel is stored for a long time. Dry storage is in no way less advantageous, and hence is the most convenient method.

The recommended method of preparation of precipitated nickel to be stored for a long time is as follows:

Nickel, precipitated from 100 ml of nickel chloride solution contain-

Table 5–10. Hydrogenation of Phenol to Cyclohexanol

Catalyst: U–Ni–BA containing 2 g of nickel, with a small amount of NaOH added

Sample: Phenol (10 g) in ethanol (50 ml)

Storage of the precipitated nickel		Hydrogenation				
Medium	Period (day)	Initial pressure (kg/cm^2)	Temperature (°C)	Time (hr)	Activity[a] (*l*)	Yield[b] (g)
air	0	66	70–110	1.0	8.6	7.9
water	6	50	76–117	1.5	7.8	8.5
„	90	75	79–120	1.5	8.0	8.2
ethanol	6	50	68–119	1.5	7.6	8.3
„	90	77	74–120	1.7	7.9	7.9
air (dry)	1	65	66–112	1.5	7.5	7.7
„	15	82	70–120	1.3	7.9	6.3

[a] Amount of hydrogen uptake, converted to 20°C, 1 atm; calculated amount 7.7 *l*. The observed values show that almost the theoretical uptake of hydrogen occurred in every experiment, taking into account some leakage of the hydrogen.

[b] Theoretical yield 10.6 g; the figures show amounts of cyclohexanol, isolated by distillation.

Table 5–11. Hydrogenation of Aromatic Compounds

Catalyst: U–Ni–BA containing 2 g of nickel, prepared from a precipitated nickel stored dry

Sample (mole)	Solvent	Initial pressure (kg/cm²)	Temperature (°C)	Time (hr)	Product	Yield (%)
benzene 0.27	none	80	90–150	2.5	cyclohexane	77
aniline 0.11	ethanol	75	150–208	3.0	*N*-ethylcyclohexylamine	69
					dicyclohexylamine	—
aniline 0.11	cyclohexane	70	150–215	3.0	cyclohexylamine	35
					dicyclohexylamine	38
pyridine 0.10	cyclohexane	65	150–218	3.0	piperidine	86

ing 40 g of $NiCl_2 \cdot 6H_2O$ and 50 g of aluminum grains (40–80 mesh), is washed well with distilled water, collected on a Buchner funnel and dried. Drying may be either under a reduced pressure or under ordinary pressure. For the latter, it is recommended that the wet precipitated nickel be heated to dryness at 100°C in an evaporating dish.

The final weight of the precipitate is about 70 g. To obtain U–Ni–BA containing 2 g of nickel, 14 g of the dry precipitate may be taken and digested with 250 g of 20% sodium hydroxide solution.

The precipitated nickel dried at a reduced pressure is rapidly oxidized with the liberation of heat if exposed to air. Although this seems to have no substantial effect upon the activity of the finished catalyst, the precipitated nickel should be kept under reduced pressure, especially for large scale storage.

Additional experiments on the hydrogenation of aromatic compounds in the presence of a catalyst prepared in this way are illustrated in Table 5–11. We can easily verify that the precipitated nickel withstands long-term storage.

This method, first devised for U–Ni–BA, turned out to be applicable to U–Ni–A and U–Ni–B as well.[36] Nickel, prepared from nickel chloride solution and zinc dust by the ordinary process, is collected on a sintered glass funnel, dried at 100°C, and left standing for a week in the air. It is subsequently treated with either 10% sodium hydroxide solution or 13% acetic acid to give U–Ni–B or U–Ni–A, the digestion process being the same as that of ordinary U–Ni catalysts. The

activities of the catalysts were tested in the high-pressure hydrogenation of acetophenone. The yield of 1–phenylethanol is very high, and the catalysts prove to be as active as those obtained from freshly prepared precipitated nickel (see Section 6. 4. 2, Table 6–15).

Nickel, precipitated either by zinc dust or aluminum, may be dried in air without fear of impairing its activity. It may be stored in air, and any required amount can be taken and treated with alkali or acid, producing a highly active catalyst. It was found that tap water is sufficient for preparing or washing the precipitated nickel, provided it does not contain catalyst poisons of any kind.

5. 6. Adsorbed Hydrogen on Urushibara Catalyst

T. Yamanaka, K. Taya, and Y. Takagi[25] have measured the amount of chemisorbed hydrogen of U–Ni–BA, investigating its connection with catalytic activity. It is known that active hydrogen on the catalyst surface is responsible for the hydrogenating ability of the catalyst. The active hydrogen is capable of reducing potassium ferricyanide to ferrocyanide, and the amount of active hydrogen available can be determined by titrating the formed ferrocyanide with potassium permanganate of known concentration.

Catalyst, prepared from 2 g of nickel chloride crystals, is added to a definite amount (about 5 times the required quantity) of 1 N potassium ferricyanide solution, which is stirred for 5 minutes at room temperature. The solid is filtered and washed well with water. The washings are added to the filtrate, which is then diluted with water to 500 ml from which 100 ml is taken, acidified with 10 ml of 20 % sulfuric acid, and titrated with 0.1 N potassium permanganate solution. In this process, 1 ml of potassium permanganate solution corresponds to 1.12 ml of active hydrogen.

The same catalyst is used in the hydrogenation of acetone. Catalyst containing 0.5 g of nickel is added to a solution of 0.025 mole (1.45 g) of acetone in 20 ml of water, and the mixture is shaken under atmospheric pressure at 55–60° C. The volume of hydrogen absorbed during the initial one hour indicates the activity of the catalyst. Pertinent data for six U–Ni–BA specimens are listed in Table 5–12. The catalysts were prepared according to Preparation 15 of Chapter 4, except that a different concentration of nickel chloride solution was employed for each catalyst. In Table 5–12, the concentration is understood to be determined by the weight of $NiCl_2 \cdot 6H_2O$ crystals. The order of

Table 5–12. Variation of Activity of U–Ni–BA According to the Amount of Adsorbed Hydrogen

Concentration of $NiCl_2$ solution (calculated as $NiCl_2 \cdot 6H_2O$)	10%	15%	20%	25%	30%	40%
Volume of 0.1 N $KMnO_4$ (ml / 0.5 g of Ni)	17.5	18.0	28.0	21.9	17.0	8.0
Volume of adsorbed active hydrogen (ml / 0.5 g of Ni)	19.6	20.2	31.4	24.5	19.1	9.0
Volume of hydrogen adsorbed in the hydrogenation of acetone (ml / 0.5 g of Ni)	127	145	239	218	131	51

activity of the catalyst is consistent with other experiments, and it turns out that the more active hydrogen that is adsorbed, the higher the hydrogenating ability of the catalyst.

The same method was applied to other catalysts, such as Raney nickel, palladium catalyst, and platinum catalyst. However, the relation between catalytic activity and amount of potassium permanganate consumed breaks down when we compare catalysts of a different sort. For example, 75 ml of 0.1 N potassium permanganate (corresponding to 84 ml of adsorbed hydrogen) is consumed by Raney nickel W–7, which contains 0.5 g of nickel. Another experiment shows that, in the presence of the same Raney catalyst, which is obtained from 1 g of Raney alloy (41% Ni), the hydrogenation of acetone is complete in 50 minutes, absorbing 607 ml of hydrogen. It is found*[1] that the hydrogen retained in Raney nickel consists of not only adsorbed hydrogen, but hydrogen formed by the reaction between the solvent water and aluminum metal remaining in the catalyst. It is also found that the method inevitably involves the oxidation of aluminum and nickel by ferricyanide.*[2]

This may also be the case with U–Ni–BA, and the values of adsorbed hydrogen listed may differ from the actual ones. The parallelism between the amount of potassium permanganate consumed and catalytic activity seems to be established, however.

Active hydrogen disappears almost completely when air is bubbled

*1) K. Tarama, T. Kubomatsu, and K. Kishida, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **82**, 1633 (1961).

*2) L. Kh. Freidlin and K. G. Rudneva, *Izvest. Akad. Nauk. SSSR, Otdel. Khim. Nauk*, **1954**, 1082; *Chem. Abst.*, **50**, 659 (1956).

into a mixture of U–Ni–BA and water for 13 hours at room temperature. The consumed volume of 0.1 N potassium permanganate reduces to only 0.9 ml per 1 g of nickel, and the hydrogenating ability is also almost completely lost. Hydrogen is not absorbed when it is employed in the hydrogenation of acetone.

6. Detailed Description of the Activities of Urushibara Catalysts

We have many kinds of Urushibara catalysts at our disposal. They closely resemble Raney catalysts in many respects, and can replace the latter for practical use. Individual Urushibara catalysts, like Raney catalysts, have their own characteristic features according to the kind of metal which is responsible for the catalytic activity, or according to the method of preparation. Much work has been devoted to the elucidation and comparison of the characteristic activities of the individual Urushibara catalysts when applied to various hydrogenations and reductions.

6. 1. Effects of Reaction Conditions under Atmospheric Pressure

The activities of U–Ni–A and U–Ni–B have been examined in the reduction of cyclohexanone to cyclohexanol in ethanol under atmospheric pressure and under various reaction conditions.[19] Each reduction was carried out at a constant temperature, and both the concentration of the sample to be reduced and the reaction temperature were varied. It is well known that, as with Raney catalyst,*1) the reduction of carbonyl compounds is facilitated by the addition of a limited amount of alkali, without which the reduction of ketones in the presence of U–Ni–A does not proceed effectively. Therefore, the amount of added alkali was also varied in this study.

In carrying out such experiments, it is necessary to prepare many aliquots of catalyst with the same activities. More reliable results are obtained when the catalyst is prepared each time under the same conditions, provided this brings about invariant activity, rather than preparing a large amount of catalyst beforehand and taking a small amount for each experiment. This is especially true in an investigation of a highly active catalyst. U–Ni catalysts are particularly advantageous for such experiments because they can be prepared in 20 minutes or less (10 minutes for U–Ni–A, and 20 minutes for U–Ni–B). This

*1) M. Delépine and A. Horeau, *Bull. Soc. Chim. France*, [5] **4**, 31, (1937).

contrasts with Raney catalysts, where the speedy preparation of catalysts of like activity meets with great difficulty, involving the addition of a solid to an alkali solution, which is necessarily accompained by the violent evolution of heat.

In this experiment, the U–Ni–B and U–Ni–A were prepared by conventional methods (Chapter 4, Preparations 3 and 4), with minor modifications to maintain constant activity. The modifications consisted of the following:

Precipitated nickel was prepared by dropping 5 ml of nickel chloride solution (containing 0.25 g of nickel) into 2.5 g of zinc dust through a pipet over a period of about 20 seconds, so that the exchange reaction could proceed at a moderate rate. The activity of the catalyst so obtained is somewhat lower than that obtained ordinarily, but it remains constant. The individually prepared catalyst was immediately employed in reduction, and it was found that the deviation in activity was less than $\pm 2.5\,\%$.

The experiment was carried out in a rocking reduction apparatus and the reactor was placed in a convenient thermostat, which controlled the temperature with several electric light bulbs. The light bulbs were screened to prevent radiant heat from reaching the vessel directly. Particular care was taken that the experiment be reproducible. It was found that there was no temperature gradient between the inner and outer parts of the vessel at an equilibrium temperature, and that the temperature rise in the vessel, due to the heat of reaction, could be confined to within 0.5°C even when the reaction proceeded at its maximum rate. The experiment was conducted in the range where the reaction rate is proportional to the amount of catalyst used. The rocking speed was 450–500 strokes per minute. It was also found that the rocking speed did not affect the reaction rate.

To secure reliable results, the following procedure was adopted: The catalyst was first mixed with the solvent and hydrogen was bubbled in with shaking. When equilibrium was reached, in which the catalyst no longer absorbed hydrogen and the temperature gradient between the reactor and thermostat disappeared, the material to be reduced, which had been dissolved in a small quantity of the solvent at the same temperature, was added all at once and the mixture was shaken immediately.* The volume of hydrogen absorbed fell off linearly with

* Delay in shaking after the addition of material will cause a reduction in catalytic activity. The activity, once damaged in this way, can not be recovered.

time,* except during the first minute of reaction. The volume of hydrogen absorbed during the first several minutes was plotted against time, and the initial rate was determined graphically by extrapolation.

(a) Concentration Dependence

Table 6–1 shows the dependence of the reduction rate upon the concentration of cyclohexanone in ethanol at 25°C under atmospheric pressure in the presence of U–Ni–B containing an amount of alkali appropriate for the reduction of ketones. It perhaps deserves to be noted that the appropriate amount of sodium hydroxide per 0.25 g nickel content of catalyst is 5 mg, which is just the quantity which remains, without any additional treatment, after the catalyst is prepared by the above-mentioned method. Reduction rates at different concentrations were obtained by performing a series of different experiments with different initial concentrations (otherwise conducted under the same conditions), rather than by analyzing a single experiment. This is because the decrease in catalytic activity during the reduction of ketones—especially cyclohexanone—is too large to be disregarded.

Table 6–1. Concentration Dependence of the Rate of Reduction of Cyclohexanone in Ethanol in the Presence of U–Ni–B

Amount of sample (mole)	Volume of solvent (ml)	Mole fraction of the sample (C) (%)	Reduction rate (k_c) (ml/min per 0.25 g Ni)	C/k_c
0.25×10^{-2}	20	0.714	3.80	0.188
0.50 „	„	1.41	4.78	0.295
1.0 „	„	2.78	5.73	0.485
1.5 „	„	4.12	6.40	0.644
2.0 „	„	5.41	6.85	0.790
3.0 „	„	7.89	7.48	1.05
4.0 „	„	10.3	7.80	1.32
6.0 „	„	14.6	8.16	1.79
8.0 „	„	18.6	8.31	2.24
8.0 „	10	31.1	8.44	3.68

* The fall-off of the reaction rate is due, in part, to the reduction in catalytic activity during the course of reaction, apart from the decrease in concentration of the material to be reduced. It is particularly remarkable in the reduction of carbonyl compounds. Formation of the product, cyclohexanol, does not affect the reaction rate.

In each run, the result was obtained by averaging several equivalent experiments. The values cited above and in the following are given for standard pressure and temperature.

The relation between the reaction rate and concentration closely resembles Langmuir's adsorption isotherm. If k_c is the reduction rate at concentration C, then the analogy leads to

$$k_c = K\frac{abC}{1+aC}$$

where a, b, and K are constants. On rearrangement, we have

$$\frac{C}{k_c} = \frac{C}{Kb} + \frac{1}{Kab}$$

which assures that C/k_c and C are linearly related. This is easily verified from Fig. 6–1, where k_c and C/k_c are plotted against concentration. We see that Kb (=8.85 ml/min per 0.25 g Ni) is the reduction rate at an infinite concentration.

It turns out that the initial rate of reduction of cyclohexanone does not fall off at any high concentration, and that the most effective reduction should occur at maximal concentration. However, as the catalytic activity falls off remarkably during reduction, too high a material-catalyst ratio would, in turn, result in hindering the completion of the reaction. Cyclohexanone is a material which greatly inhibits the ac-

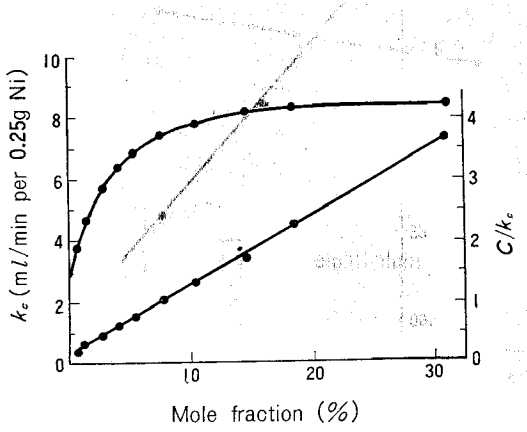


Fig. 6–1. Concentration Dependence of the Rate of Reduction of Cyclohexanone in Ethanol in the Presence of U–Ni–B

tivity of a catalyst, although at the same time it is reduced at a comparatively high rate.

Catalysts free from alkali do not show such simple relations.

(*b*) *Temperature Dependence*

Table 6–2 shows the dependence of the reduction rate of cyclohexanone in ethanol upon the temperature at which the reaction is carried out, in the presence of the same U–Ni–B as was employed in the preceding experiment. The amount of cyclohexanone is 5×10^{-3} mole, and the volume of solvent is 20 ml. The apparent activation energy is 5.3 kcal/mole. (Fig. 6–2)

Table 6–2. Temperature Dependence of the Rate of Reduction of Cyclohexanone in Ethanol in the Presence of U–Ni–B (ml/min per 0.25 g Ni)

Temp. (°C) \ Entry No.	1	2	3	4	Mean	log k_t
15	3.94	3.77	3.94	3.89	3.89	0.5899
20	4.44	4.50	4.42	4.78	4.54	0.6571
25	5.09	5.32	5.19	5.34	5.24	0.7193
30	6.29	6.08	6.18	—	6.18	0.7910

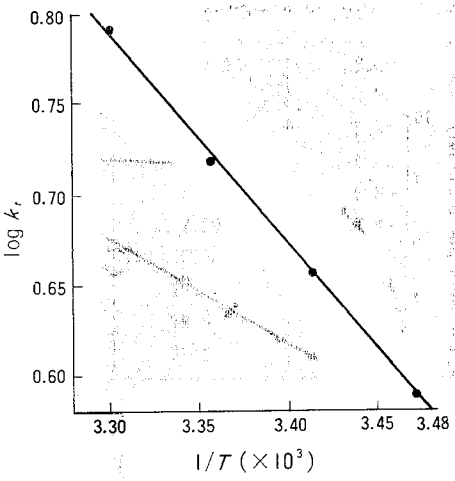


Fig. 6–2. Temperature Dependence of the Rate of Reduction of Cyclohexanone in Ethanol in the Presence of U–Ni–B

(*c*) *Dependence upon the Quantity of Alkali Added*

To investigate the effect of added alkali, it is advisable to employ U–Ni–A which is inherently free from alkali, rather than to wash U–Ni–B until it becomes neutral. Acetic acid on U–Ni–A is removed far more easily than alkali on U–Ni–B. Fig. 6–3 shows the change in the reduction rate of cyclohexanone in ethanol when a definite amount of sodium hydroxide is added to the solution in the presence of well-washed U–Ni–A. The amount of cyclohexanone present was 2×10^{-2} mole, and the volume of ethanol was 20 ml. Reduction was carried out at 25° C under atmospheric pressure. The effect of volume change due to the addition of alkali (0.2–0.4 ml) was eliminated by employing a definite volume of alkali of varying normality. The U–Ni–A employed was prepared from nickel chloride containing 0.25 g of nickel. The catalyst itself contained 0.2 g of nickel. It is found that, at first, the reduction rate increases almost linearly with the amount of alkali added. When an appropriate amount of alkali is added, it reaches a maximum and then decreases. The maximum corresponds to the point at which the solution is faintly alkaline to phenolphthalein.

Perhaps the added alkali is adsorbed on the catalyst surface and the adsorption is almost maximal when the pH of the solvent reaches the transition point for phenolphthalein. It seems that the addition of alkali is effective only when it remains on the catalyst surface, and that

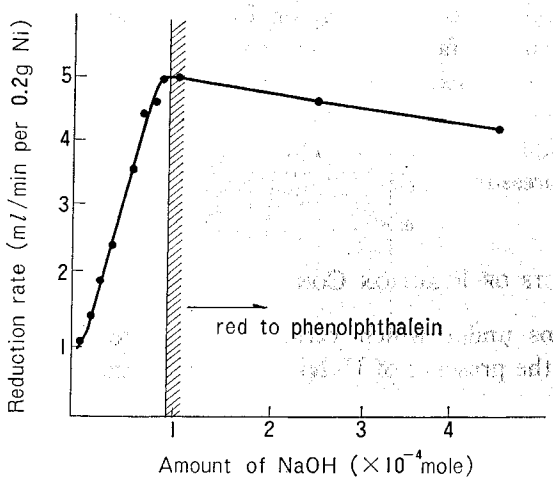


Fig. 6–3. Dependence of the Reduction Rate of Cyclohexanone on the Concentration of Alkali

Table 6–3. High-pressure Reduction of Cyclohexanone

Compound	Amount of sample (g)	Amount of sample (mole)	Amount of Ni (g)	Solvent (ml)
cyclohexanone[14]	19.6	0.2	2	ethanol 200
cyclohexanone	19.6	0.2	2	ethanol 200
benzophenone[84]	12.74	0.07	1	ethanol 110
benzophenone	12.74	0.07	1	ethanol 110

[a] Time required to complete the reaction.

alkali in the solvent decreases the reaction rate, although this does not eliminate the possibility that adsorbed sodium hydroxide, beyond a critical amount, may exert no injurious effect. Thoroughly washed U–Ni–B instead of U–Ni–A gives completely similar results. The amount of alkali required to obtain a maximum rate is almost independent of the amount of solvent present, provided it is not too great. It does, however, increase linearly with the amount of catalyst present. It has no particular relation to the concentration of the sample being reduced, but a quantitative examination has not yet been made.

The amount of sodium hydroxide required by U–Ni–A containing 0.2 g of nickel is as small as 0.004 g. To apply Urushibara nickel catalysts to the reduction of a ketone, the same amount should be added beforehand to U–Ni–A, or U–Ni–B should be washed until the wash-water is faintly alkaline to phenolphthalein. Excess alkali often results in an extraordinary depression of the reaction rate. One should remember that the values cited are those obtained at 25°C under atmospheric pressure. They may be different at other temperatures and pressures.

6. 2. Effects of Reaction Conditions under High Pressure

Conditions under which various ketones are reduced under high pressure in the presence of U–Ni–B have been examined in detail.

(*a*) *Dependence upon the Initial Pressure of Hydrogen*

Usually, high pressure reductions in the presence of Urushibara nickel catalysts are effected with an initial pressure of hydrogen in the vicinity of 50 kg/cm². Whether or not a change in the initial pressure

and Benzophenone in the Presence of U–Ni–B

pH	Initial pressure (kg/cm²)	Reaction temperature (°C)	Reaction time (min)	Product	Yield (%)
9–10	50	13–90	120	cyclohexanol	85
9–10	100	15–90	120	cyclohexanol	87
10–11	40	58–65	95[a]	benzhydrol	—
10–11	134	58–67	95[a]	benzhydrol	—

affects the reaction rate has been investigated and it was found that, in the range of initial pressure from 50 to 100 kg/cm², the rate of absorption of hydrogen was practically the same, provided the other conditions remained constant. The situation is best illustrated in Table 6–3.

(*b*) *Temperature Dependence*

Ketones are reduced at room temperature, but the rate of reduction is not very high. The application of heat brings about complete reduction in a shorter time.

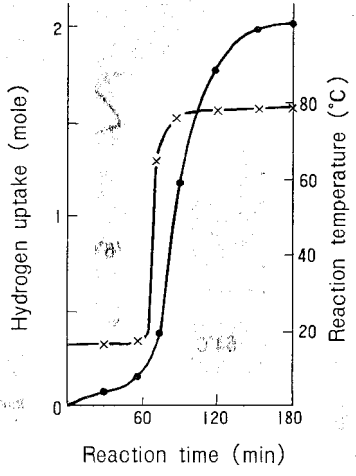


Fig. 6–4. Hydrogen Absorption Curve of Acetone (Entry No. 2, Table 6–4)

—•— hydrogen uptake; —×— temperature

Table 6–4. High-pressure Reduction in the

Entry No.	Compound	Amount of sample (g)	Amount of sample (mole)	Amount of Ni (g)	Solvent
1	acetone	11.9	0.2	2	ethanol
2	acetone	116	2	2	none
3	cyclohexanone	39.2	0.4	2	ethanol
4	acetophenone	24.0	0.2	2	ethanol
5	acetophenone	24.0	0.2	2	ethanol
6	benzophenone	18.2	0.1	2	ethanol
7	benzonitrile	15.0	0.145	3.5	ethanol

[a] The reaction was initiated at room temperature and heating was started subsequently to raise the reaction temperature.

The temperature dependence of the reduction rate has been fully examined.[14] The experimental details are shown in Table 6–4. The temperature was elevated gradually, and the volume of hydrogen absorbed was plotted at various intervals. Somewhat surprising aspects of the temperature dependence are shown in Figs. 6–4 through 6–9. The

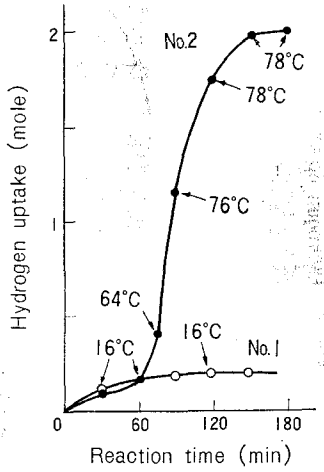


Fig. 6–5. Hydrogen Absorption Curves of Acetone (Entry Nos. 1 and 2, Table 6–4)

Presence of U–Ni–B (weakly alkaline, pH=9–10)

Initial pressure (kg/cm^2)	Temperature (°C)	Time[b] (hr)	Product	Yield (%)
50	16	2	2-propanol	—
100	64–78	1.5	2-propanol	90
50	60–90	2	cyclohexanol	82
50	18–65[a]	3	1-phenylethanol	83
50	16–114[a]	2	1-phenylethanol	86
50	60–70	1	benzhydrol	82
50	40–60	0.5	benzylamine	43
			dibenzylamine	5.6
			benzaldehyde	24.4

[b] These figures refer to the total duration of the experiment in the given temperature range; hydrogen was not necessarily being adsorbed througout the entire period.

absorption of hydrogen increases rapidly within a narrow temperature range. For example, a sharp increase is seen near 60° C in the reduction of acetone (Entry No. 2, Fig. 6–4). Fig. 6–5, which effectively compares two acetone reductions—one, a small amount of acetone at room temperature, and the other, a large amount of acetone at an elevated tem-

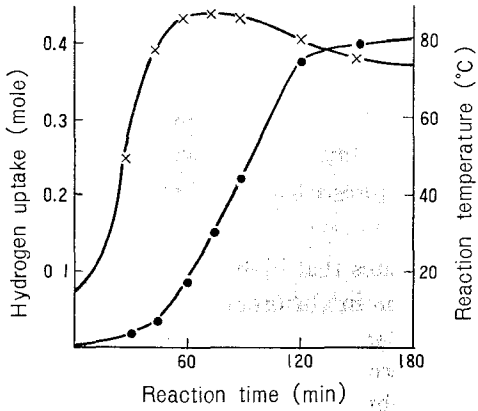


Fig. 6–6. Hydrogen Absorption Curve of Cyclohexanone (Entry No. 3, Table 6–4)

—•— hydrogen uptake; —×— temperature

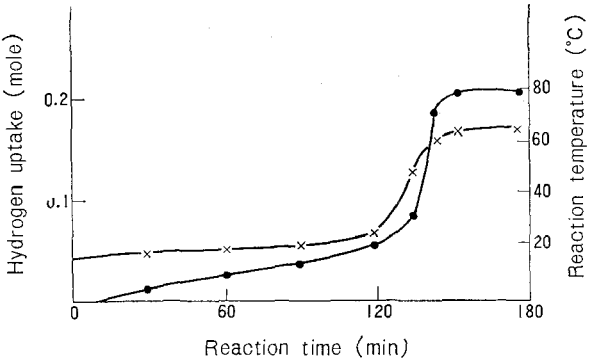


Fig. 6–7. Hydrogen Absorption Curve of Acetophenone (Entry No. 4, Table 6–4)

—•— hydrogen uptake; —×— temperature

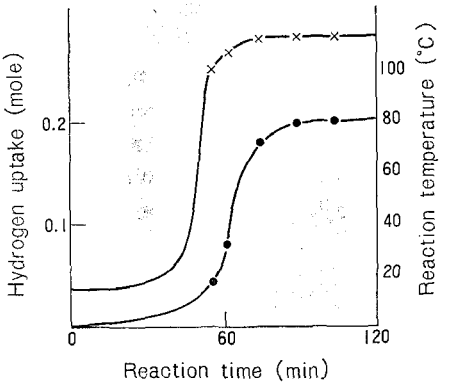


Fig. 6–8. Hydrogen Absorption Curve of Acetophenone (Entry No. 5, Table 6–4)

—•— hydrogen uptake; —×— temperature

perature—clearly indicates that high temperature is especially effective for completing reduction in a short time.

This is also true for cyclohexanone, acetophenone, and benzophenone (Figs. 6–6 to 6–9), where steep slopes are observed near 60° C.

A similar result is obtained for benzonitrile[12] (Entry No. 7). It is also reduced at room temperature, but at a low rate. The absorption curve of the material is shown in Fig. 6–10, in which a sharp increase occurs above 40° C. Here, the reaction mechanism may be somewhat

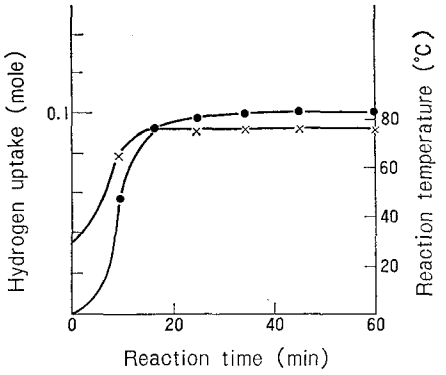


Fig. 6–9. Hydrogen Absorption Curve of Benzophenone
(Entry No. 6, Table 6–4)
—•— hydrogen uptake; —×— temperature

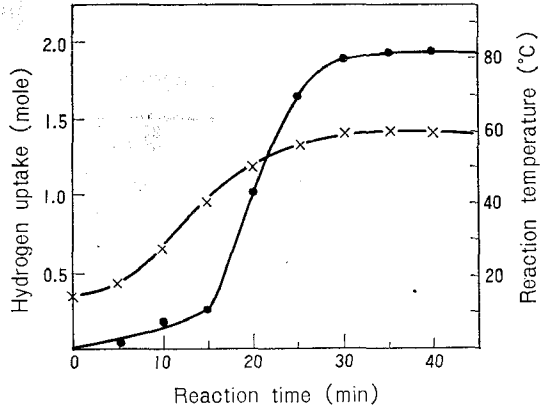


Fig. 6–10. Hydrogen Absorption Curve of Benzonitrile
(Entry No. 7, Table 6–4)
—•— hydrogen uptake; —×— reaction temperature

involved, and a considerable amount of benzaldehyde is obtained together with benzylamine and dibenzylamine. This is probably produced from aldimine after secondary hydrolysis.

(*c*) *Stepwise Reduction with Temperature Control*[14]

Benzophenone is easily reduced to benzhydrol at 60–70° C. At 160–170° C it absorbs 2 moles of hydrogen, thereby giving diphenylmethane

Table 6–5. Stepwise Reduction of Ketones in Ethanol in the

Entry No.	Compound	Amount of sample		Initial pressure (kg/cm^2)
		(g)	(mole)	
6	benzophenone	18.2	0.1	50
8	benzophenone	18.2	0.1	50
9	benzhydrol	16.4	0.09	50
10	acetophenone	24.0	0.2	50

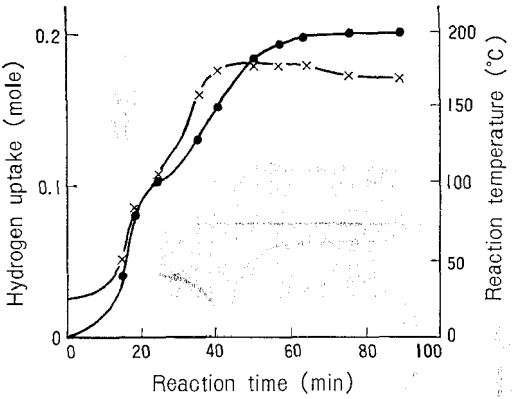


Fig. 6–11. Hydrogen Absorption Curve of Benzophenone
(Entry No. 8, Table 6–5)
—•— hydrogen uptake; —×— temperature

in an 85 % yield (Table 6–5). The hydrogen absorption curve, shown in Fig. 6–11, exhibits a shoulder near 100° C, indicating a stepwise variation in the absorption rate. It corresponds to the uptake of just one mole of hydrogen, which confirms stepwise reduction. Reduction within a temperature range of 60–80° C ensures absorption of equimolar hydrogen, the product being benzhydrol (Fig. 6–9). The reduction of benzhydrol does not take place below 100° C, but commences at a higher temperature. At 125–165° C, it absorbs another mole of hydrogen to give diphenylmethane. The reduction of benzophenone is thus stepwise; diphenlymethane is formed through benzhydrol.

Covert *et al.**1) have observed the formation of ethylcyclohexane in addition to 1-phenylethanol in the reduction of acetopheone in the

*1) L. W. Covert, R. Connor, and H. Adkins, *J. Amer. Chem. Soc.*, **54**, 1651 (1932).

Presence of U–Ni–B (2 g Ni); (weakly alkaline, pH=9–10)

Temperature (°C)	Time (hr)	Product	Yield (%)
60–70	1	benzhydrol	82
25–175	1.5	diphenylmethane	85
160–180	2.1	diphenylmethane	>60
160–180	2	1-phenylethanol	85

presence of nickel-kieselguhr catalyst. The same stepwise reduction in the presence of U–Ni–B was not observed at temperatures up to 180° C. With the latter catalyst, one mole of hydrogen is absorbed and the only product is 1-phenylethanol (Entry No. 10 in Table 6–5).

6.3. Comparison with Raney Catalysts

The Urushibara catalysts have many aspects in common with Raney catalysts, and can replace the latter in almost every reaction reported so far. Separate experiments, using one catalyst or the other, suggest that the activities of both catalysts are comparable.

Several experiments have been conducted which directly compare the activities of both catalysts. Table 6–6[18] compares the activities of U–Ni–A and U–Ni–B with that of Raney nickel in liquid-phase reduction under atmospheric pressure. The Urushibara catalysts were prepared by standard methods (Chapter 4, Preparations 3 and 4), and the Raney nickel was prepared by the method of Adkins and Billica*1)

Table 6–6. Comparison of Activities of U–Ni and Raney Ni (0.5 g Ni) during Reduction under Atmospheric Pressure

Compound	Weight of sample (g)	Solvent (ml)	Time required to complete reduction at 25°C (min)			
			U–Ni–A (Ac)[a]	U–Ni–A (Pr)[a]	U–Ni–B	Raney Ni (W–7)
sodium cinnamate	3.40	water 50	—	—	16	16
cyclohexanone	1.96	ethanol 20	40	20	44	42–50

[a] Catalysts prepared by treating precipitated nickel with acetic acid or propionic acid; 8 mg of NaOH was added in the reduction of cyclohexanone.

*1) H. Adkins and H. R. Billica, *J. Amer. Chem. Soc.*, **70**, 695 (1948); Organic Syntheses, Coll. Vol. 3, p. 179 (1955).

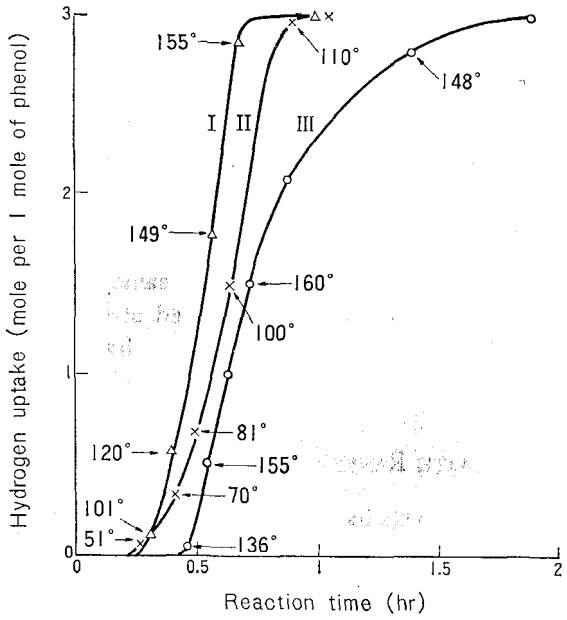


Fig. 6–12. Hydrogen Absorption Curves of Phenol

I: phenol 20 g, Raney nickel W–7 2 g, in ethanol at an initial pressure of 70 kg/cm²

II: phenol 10 g, U–Ni–BA (2 g Ni), in ethanol at an initial pressure of 66 kg/cm²

III: phenol 20 g, U–Ni–B (2 g Ni), in ethanol at an initial pressure of 70 kg/cm²

(W–7 type). The activities of the catalysts were determined in terms of the time required for the completion of the reduction of sodium cinnamate or cyclohexanone, in which the same amount of material is reduced under the same conditions in the presence of either Urushibara nickel or Raney nickel, both containing approximately the same amount of nickel. We can verify that the activities of Urushibara nickel catalysts compare with, or in some cases exceed, those of the Raney nickel catalyst.

A comparison of activities in high-pressure hydrogenation is illustrated by an experiment with phenol. Figure 6–12 shows the high-pressure reduction of phenol in ethanol in the presence of either Raney nickel (W–7), U–Ni–BA, or U–Ni–B, each containing 2 g of nickel. We see that the absorption rate of U–Ni–BA is almost the same as that

Table 6–7. Comparison of Activities of Urushibara Catalysts and Raney Nickel in the High-pressure Hydrogenation of Adiponitrile (0.1 mole) to Hexamethylenediamine

Each catalyst contains 1 g of Ni or Co.
Solvent: 40 ml of methanol
Initial pressure: 100 kg/cm²

Catalyst	Temperature (°C)	Time (min)	Yield (%)
U–Ni–B	128	60	57
U–Ni–NH_3	124	30	73
U–Co–B	96	55	80
Raney nickel	110	25	75

of Raney nickel. The rates of U–Ni–B and Raney nickel are comparable in the initial stages, but an appreciable retardation is observed in the former in the final stages. The comparison, however, is not entirely rigorous, because the reaction temperature can not be fixed for all of the experiments, since the absorption of hydrogen begins at different temperatures.

Table 6–7 shows the high-pressure reduction of adiponitrile in the presence of these catalysts.[30] It can be seen that U–Ni–B is somewhat inferior to Raney nickel, but U–Ni–NH_3 has a comparable activity.

6. 4. Aspects of Individual Urushibara Catalysts

There are many kinds of Urushibara catalysts. Of the various Urushibara nickel catalysts, which have been modified successively from the outset, U–Ni–A, U–Ni–B, and U–Ni–BA are representative; their activity is comparable to that of Raney nickel in many reductions. Urushibara cobalt and Urushibara copper are peculiar catalysts which resemble Raney cobalt and Raney copper respectively.

Many experiments have been devoted to investigating the characteristic activities of individual Urushibara catalysts, by employing them in the hydrogenation of the same material. The activities were compared in terms of the rate of reduction of ketones under high pressure. Either the temperature at which the absorption of hydrogen begins, the time required for complete hydrogenation, or the amount of catalyst necessary for the completion of reduction is also a measure of the activity of the catalyst.

6. 4. 1. Urushibara Nickel, Urushibara Cobalt and Urushibara Copper

The activities of Urushibara catalysts prepared in different ways were compared with each other in the high-pressure hydrogenation of benzophenone to benzhydrol.[34] The time required for completion was regarded as a measure of activity. Reduction was effected in a 200 ml autoclave equipped with a magnetic stirrer. The catalyst, containing 1 g of nickel, cobalt, or copper, was carefully transferred into the autoclave with ethanol, the air in the autoclave being completely driven out by hydrogen. The following conditions were always employed except for special cases: (1) sample: benzophenone, 12.74 g (0.07 mole); (2) solvent: ethanol (99%), 110 ml; (3) pH: 9–11; (4) agitation frequency: 40–50 strokes per minute; (5) temperature: 58–70°C.

Agitation was started when the lower temperature limit was reached, since the reduction had already begun to take place at that temperature (see Section 6. 2 (*b*)).

The pressure was measured every five minutes. When the reaction was over, the mixture was allowed to cool, and the hydrogen was discharged. The contents were washed down with ethanol and filtered. The solid was washed with another portion of ethanol which was combined with the filtrate. The major portion of the solvent was distilled

Table 6–8. Reduction of Benzophenone[a] in the Presence

Entry No.	Catalyst[b]	Source material	pH
11	U-Ni-B	$NiCl_2$	10.2
12	U-Ni-B	„	11.1
13	U-Ni-B	„	8.9
14	U-Ni-B[d]	„	8.3
15	U-Ni-B[e]	„	11
16	U-Ni-B	$Ni(CH_3CO_2)_2$	10.8
17	U-Ni-B	„	11.3
18	U-Ni-B[f]	„	10.6
19	U-Co-B	$CoCl_2$	10.1

[a] Benzophenone was purified by a single vacuum distillation.
[b] Containing 1 g of either Ni or Co.
[c] Weight of catalyst, dried after the reaction.

off and the hot residue was poured into 300 ml of hot water with stirring. The crude benzhydrol was filtered and dried, and recrystallized from ligroin into silky needles, m.p. 68–69°C. In every reduction the yield was 90–95% of the theoretical amount.

(*a*) *Ordinary Urushibara Nickels and Urushibara Cobalts*

In Tables 6–8 through 6–10, the activities of various nickel and cobalt catalysts, prepared either by different methods or from different sources, are compared. The first and second involve the reduction of benzophenone which was purified by a single vacuum distillation. Table 6–8 demonstrates that the activity is almost independent of the initial pressure of hydrogen within the range of 30–134 kg/cm^2. Hence the pressure effect is ignored in the following.

An inspection of these tables gives an insight into several detailed aspects of the individual catalysts. Potassium hydroxide can be used in place of sodium hydroxide for digesting the precipitated nickel with no depression of activity (Entry No. 14). U–Ni–B, prepared with a smaller amount of zinc dust and a greater amount of alkali shows a somewhat lower activity (Entry No. 15). The latter may be due partly to the fact that the nickel particles have grown larger, and partly to the prolonged contact with alkali, which may injure the surface. The catalyst contains smaller amounts of zinc and zinc oxide, which may

of Various U–Ni–B and U–Co–B Catalysts

Total weight of catalyst[e] (g)	Initial pressure (kg/cm^2)	Initial temperature (°C)	Working temperature (°C)	Time (min)
	40	20	58–65	95
	134	22	58–67	95
6.7	30	29	58–67	95
	50	26	58–64	100
	50	17	59–76	165
9.5	45.5	20	58–66	55
	35	23	58–64	55
9	65	25	58–66	65
	55	26	58–68	95

[d] Prepared by treating the precipitated nickel with 200 g of 14% KOH.

[e] Prepared by treating the precipitated nickel (obtained by the use of 5 g of zinc dust) with two 150 g aliquots of 10% NaOH.

[f] Prepared by treating the precipitated nickel with 150 g of 20% NaOH.

Table 6–9. Reduction of Benzophenone[a] in the

Entry No.	Catalyst[b]	Source material	pH
21	U-Ni-B[d]	$Ni(CH_3CO_2)_2$	7.5
22	U-Co-B[d]	$CoCl_2$	7.7
23	U-Ni-A	$NiCl_2$	7
24	U-Ni-A	$Ni(CH_3CO_2)_2$	6.8
25	U-Co-A	$CoCl_2$	6.7

[a] Benzophenone was purified by a single vacuum distillation.
[b] Containing 1 g of either Ni or Co.

act as a carrier of the catalyst.[10] Note that the catalysts obtained from nickel acetate (Entry Nos. 16, 17, and 18) are about three times as bulky as that from nickel chloride, weighing 8.5–10.5 g (dry weight per 1 g of Ni), and are more active than the latter. Results of experiments with more carefully purified benzophenone are inconsistent, however, so that it appears the carriers are perhaps particularly effective for somewhat impure materials.

Table 6–9 is a picture of the activity in the absence of alkali, which, as we have seen, accelerates the reduction of carbonyl compounds (see Section 6. 1 (*c*)[19]). The table shows the results of the reduction with U–Ni–A in neutral solution, and with thoroughly washed U–Ni–B. It clearly indicates that reduction should occur above pH 8. (S. Nishimura[19] reported that too great a quantity of alkali would inhibit reduction, however.)

The reduction of an extremely pure sample of benzophenone is illustrated in Table 6–10. For this experiment benzophenone was recrystallized twice from ethanol after distillation in vacuo (b.p. 140–141°C/5 mm., m.p. 48°C). We note that the reaction rate is remarkably enhanced with U–Ni–B.

The table also indicates that U–Ni–BA, which is so distinguished in effecting aromatic hydrogenation,[31] gives rather poor results (Entry Nos. 37, 38). U–Co–BA also proves to be less active (Entry No. 39); it requires a higher reaction temperature and a longer reaction time.

The activity of U–Ni–A is striking, provided a very small amount of alkali is added to it (Entry Nos. 310–313). This appears to be due partly to the smaller bulk of the catalyst, which facilitates the dispersion of the catalyst in the liquid when it is agitated. U–Ni–A obtained

Presence of Various Catalysts in Neutral Solution

Total weight of catalyst[c] (g)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
	45	20	58–66	250
6.6	55	22	58–66	165
	55	22	58–64	155
0.7	45	18	62–102	205
	50	20	62–76	180

[c] Weight of catalyst, dried after the reaction.
[d] Thoroughly washed with water to remove all traces of alkali.

Table 6–10. Reduction of Extremely Pure Benzophenone[a] in the Presence of Various Urushibara Catalysts

Entry No.	Catalyst[b]	pH	Total weight of catalyst[c] (g)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
31	U-Ni-B	9.7	6.5	30	24	58–68	75
32	U-Ni-B	9.3	6.8	49.5	22	63–67	25
33	U-Ni-B	9.4	6.6	52.5	28	61–66	35
34	U-Ni-B[d]	11.1	11.2	50	16	63–66	30
35	U-Co-B	10.4	7	50	15	60–69	70
36	U-Co-B	9	6.2	56	24	61–65	65
37	U-Ni-BA	10.5	1.4	50	15	60–64	45
38	U-Ni-BA	10.6	1.8	45	14	62–66	35
39	U-Co-BA	10.2	0.8	45	16	72–84	115
310	U-Ni-A	10.5[e]	1.1[f]	52	25	60–63	10
311	U-Ni-A	10.3[e]	1.4[f]	46	26	59–62	8
312	U-Ni-A	10.1[e]	1.4[f]	48.5	20	59–63	6
313	U-Ni-A	10[e]	1.3[f]	46	29	60–62	12
314	U-Ni-A[d]	10.4[e]	0.7	45	24	59–66	60
315	U-Co-A	10.1[e]	1[f]	45	22	61–66	45
316	U-Co-A	10.4[e]	1.2[f]	49.5	25	59–65	50

[a] Benzophenone was purified by a single vacuum distillation, followed by recrystallization twice from ethanol.
[b] Containing 1 g of either Ni or Co.
[c] Weight of catalyst, dried after the reaction.
[d] Prepared from nickel acetate. Other nickel catalysts were prepared from nickel chloride.
[e] 0.5 ml of 10% NaOH was added.
[f] Containing 0.75–0.85 g of either Ni or Co.

from nickel acetate, however, is rather less active than U–Ni–B obtained from the same source (Entry No. 314), for which no reason can be given as yet.

U–Co–A, when used in the presence of a very small amount of alkali, seems more active than U–Co–B (Entry Nos. 315, 316).

(*b*) *U–Ni–A of Low Activity*

It sometimes happens that a catalyst of low activity is preferred for a particular purpose. Thus, a low-activity U–Ni–A catalyst is prepared in a similar way to highly active U–Ni–A, except that digestion is interrupted before the solution turns green (see Preparation 4, Chapter 4). The results of the reduction of benzophenone with such catalysts are presented in Table 6–11. It can be seen that the activity of such a catalyst is considerably lower than that of ordinary U–Ni–A, and that a higher concentration of sample to be reduced or a larger amount of catalyst facilitates the reduction.

Table 6–11. Reduction of Benzophenone[a] in Ethanol in the Presence of U–Ni–A of Intentionally Low Activity

Entry No.	Weight of catalyst[b] (g)	pH[c]	Weight of sample (g)	Volume of ethanol (ml)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
1	1	10.7	12.74	110	45	16	60–66	30
2	2	10	12.74	110	40	22	62–66	10
3	1	10.1	12.74	55	32	20	60–68	10
4	1	10.2	25.48	110	60	14	61–66	20
5	1	10.2	12.74	110	50	20	97–100	7
6	1	10.5	12.74	55	45	18	98–108	4

[a] Benzophenone was purified by a single vacuum distillation, followed by recrystallization twice from ethanol.

[b] Weight of Ni metal contained in catalyst.

[c] 0.5 ml of 10% NaOH was added.

(*c*) *U–Ni–C and U–Co–C*

In Table 6–12, the activities of U–Ni–CA, U–Ni–CB, U–Co–CA, and U–Co–CB are compared with each other in the reduction of benzophenone. These catalysts are prepared by carrying out the ion-exchange reaction at room temperature or with cooling so that the

Table 6–12. Reduction of Benzophenone[a] in the Presence of Various Urushibara-C Catalysts

Entry No.	Catalyst[b]	pH	Total weight of catalyst[c] (g)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
1	U-Ni-CB[d]		5.7	34.5	16	62–65	35
2	U-Ni-CB[d]	10.2	11.5	56	22	60–62	20
3	U-Ni-CB[e]	10.7	8.8	60	25	60–66	15
4	U-Ni-CB[e]	10	9.6	50	22	68–70	10
5	U-Ni-CA[d]	10.1[f]	0.55	40	14	66–70	15
6	U-Ni-CA[d]	10.5[f]	0.55	42	13	62–66	10
7	U-Ni-CA[d]	10.3[f]	0.7	50	17	63–65	20
8	U-Ni-CA[d]	10[f]	0.7	50	20	60–63	15
9	U-Ni-CA[d]	10[f]		60	26	61–65	10
10	U-Ni-CA[e]	10.2[f]	0.6	52.5	20	62–64	10
11	U-Ni-CA[e]	9.8[f]	0.5	42.5	24	58–60	30
12	U-NiC-A[e]	10[f]		55	24	62–66	15
13	U-Co-CB[d]	10.5	8.5	60	20	60–62	35
14	U-Co-CB[d]	10.5	7.8	40	23	59–60	35
15	U-Co-CB[e]	10.6	3.4[g]	60	20	62–66	35
16	U-Co-CB[e]	10.2	3.2[g]	52	28	60–66	35
17	U-Co-CA[d]	10.7[f]	1.1	55	22	60–64	30
18	U-Co-CA[e]	10.6[f]	1.4	55.5	23	60–62	60[h]
19	U-Co-CA[d]	10.4[f]	1.4	37	22	59–62	80[h]

[a] Benzophenone was purified by a single distillation, followed by recrystallization twice from ethanol.

[b] Containing 1 g of either Ni or Co.

[c] Weight of catalyst, dried after the reaction.

[d] The precipitated metal was prepared at room temperature.

[e] The precipitated metal was prepared under ice cooling.

[f] 0.5 ml of 10% NaOH was added.

[g] The precipitated cobalt was digested for 1.5 hr under ice cooling.

[h] After reduction, most of the catalyst deposits on the flange of the copper packing.

precipitated metal separates out finely and uniformly on the surface of the zinc dust. It is generally admitted that a catalyst owes its activity mainly to the fineness of the particles, which in turn, is decided by the particle size of the precipitated metal. Urushibara catalysts made from finely precipitated metal are indeed more active than ordinary catalysts. One exception is U–Ni–CA, which requires a somewhat

Table 6–13. Reduction of Benzophenone[a] in the Presence of Various Urushibara Copper Catalysts

Entry No.	Catalyst[b]	pH[c]	Total weight of catalyst[d] (g)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
1	U-Cu	10	2.2	40	16	100–118	40
2	U-Cu	9.5	2.4	53	24	110–120	65
3	U-Cu-C	10.3	4.2	50	28	110	10
4	U-Cu-C		2.8	52.5	22	120–121	15

[a] Benzophenoe was purified by a single vacuum distillation, followed by recrystallization twice from ethanol. Solvent for reduction was 55 ml of ethanol.
[b] Containing 1 g of copper.
[c] 0.5 ml of 10% NaOH was added.
[d] Weight of catalyst, dried after the reaction.

longer time to complete reduction than does ordinary U–Ni–A, but is in no way poorer than the other catalysts.

(*d*) *Urushibara Copper*

The activity of the Urushibara copper catalyst is shown in Table 6–13. It is lower than that of the nickel catalyst; the situation very much resembles that of Raney copper*1). It must be remembered that U–Cu–B is almost useless, since the precipitated copper scarcely reacts with sodium hydroxide solution in concentrations of 10% or greater; hence treatment with the latter is meaningless. Here again, U–Cu–C is more active than ordinary U–Cu.

There is another experiment[37] involving the reduction of benzoin and bezil in the presence of U–Cu–C (see Tables 6–17 and 6–18 below). The reduction temperature must be somewhat higher than that for U–Ni, but the activity is satisfactory at that temperature.

6. 4. 2. Particular Urushibara Nickel Catalysts

Urushibara nickel catalysts are produced from precipitated nickel. Usually the precipitated nickel is freshly prepared whenever required. Precipitated nickel which is dried and stored for a long time in air also gives a Urushibara catalyst whose activity is by no means poorer. Waste

*1) L. Faucounau, *Bull. Soc. Chim. France*, [5] **4**, 58 (1937).

catalyst can also be regenerated with excellent results using suitable treatment.

The activities of these catalysts have been compared with each other in the high-pressure reduction of acetophenone to 1-phenylethanol.[36] Reduction was carried out under similar conditions in the presence of the catalysts, each containing 1 g of nickel, and the time required for completion of the reduction was regarded as a measure of the activity.

The catalyst was carefully transferred with ethanol to a 200 ml autoclave equipped with a magnetic stirrer, and the air was completely replaced by hydrogen. The following conditions were always employed: (1) sample: acetophenone (purified by repeated freezing), 30 g (0.25 mole); (2) solvent: ethanol, 60 ml; (3) pH: 9–11 (1 ml of 10% sodium hydroxide solution was added to U–Ni–A and U–Ni–CA); (4) agitation frequency: 40–45 strokes per minute; (5) temperature: 60–70°C.

Agitation was begun when the lower temperature limit was reached, and the temperature was kept within the range specified. Most experiments were carried out at an initial pressure around 50 kg/cm², because it has been found that the initial pressure is almost immaterial up to 100 kg/cm² for a precise determination of the reaction rate.[34] Hydrogen was recharged whenever the pressure dropped to 20–30 kg/cm², and the reduction continued until the hydrogen uptake ceased. The pressure was measured every five minutes.

When the reaction was complete, the catalyst was filtered and washed with ethanol, which was combined with the filtrate. Most of the solvent was distilled off and the residual liquid was distilled under reduced pressure. The fraction which distilled at 89–91°C/15 mm Hg was collected. The yield of 1-phenylethanol was 91–95% of the theoretical in every case.

(*a*) *Usual Urushibara Nickel Catalyst*

For convenience of comparison, the results of the reduction of acetophenone with the usual Urushibara nickel catalysts are presented as a standard in Table 6–14. The general aspect very much resembles that pictured in the foregoing section, which involves the reduction of benzophenone. A slight difference exists in that U–Ni–B obtained from nickel acetate and U–Ni–BA show somewhat lower activities compared with the latter case[34] (Entry Nos. 15 through 18).

Table 6–14. Reduction of Acetophenone in the Presence of Various Urushibara Nickel Catalysts

Entry No.	Catalyst[a]	pH	Total weight of catalyst[b] (g)	Initial pressure (kg/cm²)	Total pressure depression[c] (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
11	U-Ni-B	10	7.3	45	56.5	22	61–70	125
12	U-Ni-B	9.7	8.6	50	54.5	23	60–70	90
13	U-Ni-B	9.3	7.4	47	57	22	61–70	80
14	U-Ni-B	9	7.5	46	52	21	62–70	70
15	U-Ni-B[d]	10.6	10.5	42	59	25	62–70	105
16	U-Ni-B[d]	10.5	10.8	45	55	21	60–70	105
17	U-Ni-BA	9.4	1.2	40.5	51	25	61–70	120
18	U-Ni-BA	10.4	1.1	45	50	23	62–70	95
19	U-Ni-CB	9.7	7	49.5	56.5	22	63–66	65
110	U-Ni-CB	10.4	9.2	50	63	21	61–66	60
111	U-Ni-CB	10.7	8.4	49	71	30	64–69	50
112	U-Ni-A	9.5[e]	1.3	47	54.5	24	60–68	40
113	U-Ni-A	10[e]	1.3[f]	45	51.5	24	60–68	35
114	U-Ni-A	9.8[e]	1.3	46	50	24	61–68	35
115	U-Ni-A	9.2[e]	1.3[f]	49	55.5	24	62–70	25
116	U-Ni-CA	9.5[e]	0.9[g]	42	49.5	20	62–69	50
117	U-Ni-CA	9.6[e]	0.8[g]	47.5	55.5	20	62–66	50
118	U-Ni-CA	9.4[e]	0.6	49	51	17	65–70	40
119	U-Ni-CA	9.4[e]	0.7	44	46.5	22	61–69	40

[a] Containing 1 g of Ni.
[b] Weight of catalyst, dried after the reaction.
[c] Recharged several times with supplemental amounts of hydrogen.
[d] Prepared from nickel acetate.
[e] 1 ml of 10% NaOH was added.
[f] Nickel content about 0.83 g.
[g] Nickel content about 0.57 g.

(*b*) *Urushibara Nickel Catalysts Obtained from Stored Precipitated Nickel*

As mentioned earlier, precipitated nickel to be used in the preparation of U–Ni–BA can be stored for a long time without loss of activity in the catalysts prepared.[31] This was also found to be the case for U–Ni–B and U–Ni–A,[36] as is amply supported by Table 6–15. This table shows results of the reduction of acetophenone in the presence of U–Ni–B or U–Ni–A, which were prepared according to Preparations

Table 6–15. Reduction of Acetophenone in the Presence of Various Urushibara Nickel Catalysts, Prepared from a Stored Precipitated Nickel[a]

Entry No.	Catalyst[b]	pH	Total weight of catalyst[c] (g)	Initial pressure (kg/cm^2)	Total pressure depression[d] (kg/cm^2)	Initial temperature (°C)	Working temperature (°C)	Time (min)
21	U-Ni-B	9.2	9	48	57	32	60–69	85
22	U-Ni-B	9.3	8.6	47	55	24	60–68	50
23	U-Ni-A	9.4[e]	1.2	48	53.5	27	60–68	35
24	U-Ni-A	9.7[e]	1.3	50	52.5	25	61–65	40

[a] The precipitated nickel was prepared from nickel chloride solution and zinc dust. It was washed with water, dried at about 100°C, and left standing for a week in air.

[b] Containing 1 g of Ni.

[c] Weight of catalyst, dried after the reaction.

[d] Recharged twice with supplemental amounts of hydrogen.

[e] 1 ml of 10% NaOH was added.

3 and 4, Chapter 4, with the modification that the precipitated nickel was dried at about 100°C and stored for a week in air. Moreover, the table also confirms that air need not be excluded from the precipitated nickel, in spite of the earlier belief that the latter must be stored under reduced pressure.

(*c*) *Regenerated Urushibara Nickel Catalysts*

The regeneration of used catalysts is advantageous in that the time and cost of preparation are largely saved. In this respect, the activities of regenerated catalysts have been examined in detail. We shall first summarize the regeneration processes which will be referred to below in Table 6–16. The used catalyst is recovered by filtration after reaction, dried at about 100°C, and stored.

(A) Recovered U–Ni–A (1.3 g) was mixed well with zinc dust (5 g) and water (3 ml), to which 80 g of 10% sodium hydroxide solution was added. The mixture was heated to 50–55°C for 20 minutes with occasional stirring, then to 75–80°C for 5 minutes, after which the evolution of hydrogen subsided and grayish white zinc compounds were deposited. The supernatant liquor was decanted and the residual solid was washed with 200 ml of hot water, and then with two 50 ml portions of ethanol. Each time the washing was decanted.

Table 6–16. Reduction of Acetophenone in the Presence

Entry No.	Catalyst	Parent catalyst	Method of regeneration (see text)	Total weight of catalyst[b] (g)
31	U-Ni-B	U-Ni-A	A	5.7
32	U-Ni-A	U-Ni-A	B	1.1
33	U-Ni-A	U-Ni-A	C	0.9[d]
34	U-Ni-A	U-Ni-A	D	1.1
35	U-Ni-A	U-Ni-B	E	1.1[e]
36	U-Ni-A	U-Ni-CB	F	0.8[d]
37	U-Ni-A	U-Ni-A	G	0.9
38	U-Ni-A	U-Ni-A	H	0.9
39	U-Ni-A	U-Ni-A	I	0.8

[a] 1 ml of 10% NaOH was added in all runs except for Entry No. 31.
[b] Weight of catalyst, dried after the reaction.
[c] Recharged twice with supplemental amount of hydrogen.

(B) U–Ni–A (1.3 g), recovered from Entry No. 113 (Table 6–14) and stored for 55 days, was mixed well with zinc dust (10 g) and water (5 ml), to which 160 g of 13% acetic acid was added. As the vigorous evolution of hydrogen occured soon after the addition of acetic acid, careful agitation by hand was necessary to prevent the contents from running over. After about 5 minutes, the solution turned green, but the solid did not come to the surface. The solid was collected on a sintered glass filter and washed with 200 ml of water, then with 100 ml of ethanol.

(C) U–Ni–A (1.1 g), recovered from Entry No. 32 (Table 6–16), was mixed with zinc dust (5 g) and water (3 ml), to which 80 g of 13% acetic acid was added. Subsequent treatment was the same as in (B). A very fine catalyst was obtained.

(D) Recovered U–Ni–A (1.4 g) was mixed with zinc dust (2.5 g) and water (2.5 ml), to which 40 g of 13% acetic acid was added. Subsequent treatment was the same as in (B).

(E) U–Ni–B (7.3 g), recovered from Entry No. 11 (Table 6–14), was treated as it stood with 160 g of 13% acetic acid until solid matter came to the surface of the solution, which turned green. Little hydrogen was given off. The solid was collected on a sintered glass filter and washed with 200 ml of water, then with 100 ml of ethanol.

(F) U–Ni–CB (7 g), recovered from Entry No. 19 (Table 6–14),

of Various Regenerated Urushibara Nickel Catalysts[a]

Initial pressure (kg/cm^2)	Total pressure depression[c] (kg/cm^2)	Initial temperature (°C)	Working temperature (°C)	Time (min)
49.5	59	21	60–64	130
50.5	50	14	65–69	30
45.5	51.5	20	61–64	45
47	52	18	60–64	40
46	55.5	21	60–68	45
46.5	52.5	26	63–69	60
47.5	55.5	26	60–64	40
48	55.5	22	61–63	40
48.5	54.5	20	60–65	45

[d] Nickel content about 0.5 g.
[e] Nickel content about 0.7 g.

was treated with 160 g of 13% acetic acid. The generation of hydrogen was scarcely observed and the liquid looked black due to a suspension of fine solids. After about 8 minutes, the solid was centrifuged from the green-colored liquid and washed with two 200 ml portions of water, then with two 50 ml portions of ethanol. Each time the washing was decanted from the centrifuge tube.

(G) Recovered U–Ni–A (1.4 g) was mixed with water (2 ml) and 50 g of 20% acetic acid was added. It was left standing for one minute at 70–75°C on a boiling water bath. A vigorous reaction took place at this temperature, accompanied by the evolution of hydrogen, and a solid came to the surface of the green solution. The solid was collected on a sintered glass filter and washed with 200 ml of water, then with 100 ml of ethanol.

(H) Recovered U–Ni–A usually weighs 1.3–1.4 g per 1 g of nickel content. U–Ni–A (0.9 g) recovered from Entry No. 37 (Table 6–16) was supplemented with 0.5 g of another specimen of recovered U–Ni–A, which had been stored for a long time. This was mixed with 2 ml of water and then treated, following procedure (G).

(I) Treatment was the same as in (G), except that 10% acetic acid was used instead of 20%, and the temperature was 75–80°C.

In all of the above processes, distilled water was used for washing and air was very carefully excluded from the finished catalysts.

Table 6–16 illustrates the activities of these regenerated catalysts in the reduction of acetophenone. It proves that they are in no way less active than ordinary catalysts. U–Ni–B regenerated from a U–Ni–A and zinc dust (Entry No. 31) shows only an insignificant depression in activity, whereas U–Ni–A regenerated from the same source (Entry No. 32) proves to be more active than its parent catalyst. One possible reason may be that an injurious substance on the catalyst surface is removed by the hydrogen generated from the zinc dust and alkali or acid, the latter being more exhaustive.

Moreover, zinc dust may be reduced in amount (Entry Nos. 33 and 34), or even dispensed with (Entry Nos. 35 and 36), in the process of regeneration—in the former cases the amount of zinc dust to be added can be reduced by a factor of one-half or one-fourth; in the latter cases, the amount of zinc dust originally present in the parent U–Ni–B or U–Ni–CB is sufficient for regeneration. It is interesting to note that U–Ni–A, which contains hardly any zinc, also gives rise to as good a catalyst when treated with acetic acid under appropriate conditions without the further addition of zinc (Entry Nos. 37, 38, and 39). In this case, nickel itself reacts vigorously with the acid.

6. 4. 3. Urushibara Nickel Catalysts Prepared by the Simplified Method

Along with the reductions of benzophenone[34] and acetophenone,[36] we have information on the catalytic reductions of benzoin and benzil.[37] An experiment was carried out to determine the activities of various Urushibara catalysts, with particular emphasis on those prepared by the simplified method. The method involves preparing precipitated nickel from zinc dust and crystals of nickel chloride, instead of its solution (Preparations 10 and 11, Chapter 4). Table 6–17 and 6–18 compare the activities of U–Ni–A and U–Ni–B and their simplified analogs, together with U–Ni–CB and U–Ni–A(HCl) (Preparation 13), each containing 0.5 g of nickel. The U–Cu catalyst, which contains 1 g of copper, is also included for convenience. The catalysts were carefully transferred to a 100 ml autoclave equipped with a magnetic stirrer, and the air was completely replaced by hydrogen. The following conditions were employed in most cases: (1) sample: benzoin (recrystallized three times from ethanol, m.p. 133–134°C), 10.6 g (0.05 mole) or benzil (recrystallized from methanol, m.p. 96.5–97°C), 10.5 g (0.05 mole); (2) solvent: ethanol (99%), 50 ml; (3) pH: 9–11 (0.5 ml of 5% sodium hydroxide solution was added to U–Ni–A, U–Ni–CA,

Table 6–17. Reduction of Benzoin in the Presence of Various Urushibara Nickel and Copper Catalysts

Sample: 10.6 g (0.05 mole) of benzoin in 50 ml of ethanol (99%)

Entry No.	Catalyst[a]	Total weight of catalyst[b] (g)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time (min)
11	U-Ni-B	3.5	59	22	60–61	100
12	U-Ni-B	3.3	55	16	60–65	50
13	U-Ni-B(s)	2.8	64	30	60–66	60
14	U-Ni-B(s)	2.6	54	20	60–64	50
15	U-Ni-CB	5.5	60	30	60–61	50
16	U-Ni-CB	4.6	60	26	61–63	17
17	U-Ni-A[c]	0.7	55	21	65–67	10
18	U-Ni-A[c]	0.6	60	23	60–64	20
19	U-Ni-A(s)[c]	0.4	67	26	62–64	35
110	U-Ni-A(s)[c]	0.5	57	23	61–64	25
111	U-Ni-A(HCl)[c]	0.25	53	28	60–66	115
112	U-Ni-A(s)(HCl)[c]	0.3	56	26	62–64	85
113	U-Cu-C[c, d]	2.3	38	23	130–132	30

[a] Containing 0.5 g of Ni or 1 g of Cu.
[b] Weight of catalyst, dried after the reaction.
[c] 0.5 ml of 5% NaOH was added.
[d] Prepared by the modified method, Preparation 29, Chapter 4.

and U–Cu–C); (4) agitation frequency: 40–45 strokes per minute; (5) temperature: 60–68°C (130°C for U–Cu–C).

Agitation was begun when the lower temperature limit was reached, and the temperature was kept within the range cited throughout the operation. The time required for the temperature to reach 60°C was 30–35 minutes for all runs. Here also any difference in initial pressure may be disregarded up to 100 kg/cm². The pressure was measured every five minutes.

When the reaction was complete, the catalyst was filtered off together with any crystals which happened to separate out, and washed with hot ethanol to dissolve the latter. From the combined filtrate, most of the solvent was distilled off and the hot residue was poured into hot water with stirring. After cooling, the crude hydrobenzoin was filtered and dried. It was recrystallized from the ethanol-water mixture into colorless scales, m.p. 139–140°C. Yield: 90–93% of the theoretical.

Table 6–18. Reduction of Benzil in the Presence of Various Urushibara Nickel and Copper Catalysts

Sample: 10.5 g (0.05 mole) of benzil in 50 ml of ethanol (99%)

Entry No.	Catalyst[a]	Total weight of catalyst[b] (g)	Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time[c] (min)
21	U-Ni-B	3.4	93	22	60–64	120 (45, 75)
22	U-Ni-B	4.9	96	26	60–68	165 (60, 105)
23	U-Ni-B(s)	—	80.5	30	60–66	75 (20, 55)
24	U-Ni-B(s)	2.8	90	23	60–65	100 (35, 65)
25	U-Ni-CB	5.6	97.5	25	63–66	35 (10, 25)
26	U-Ni-CB	4.2	101	26	59–66	95 (20, 75)
27	U-Ni-A[d]	0.65	95	20	60–66	25 (10, 15)
28	U-Ni-A[d]	0.7	84	20	58–61	110 (40, 70)
29	U-Ni-A(s)[d]	0.35	42.5[e]	23	60–68	55 (20, 35)
210	U-Ni-A(s)[d]	0.35	42[e]	22	60–66	90 (30, 60)
211	U-Cu-C[d, f]	2.3	80	24	128–138	55 (20, 35)

[a] Containing 0.1 g of Ni or 1 g of Cu.

[b] Weight of catalyst, dried after the reaction.

[c] The first value in parentheses indicates the time required to reduce one carbonyl group; the second indicates the time required to reduce the second carbonyl group. Values outside the parentheses show the total time.

[d] 0.5 ml of 5% NaOH was added.

[e] Recharged with supplemental amounts of hydrogen three times when the pressure dropped to 30 kg/cm².

[f] Prepared by the modified method, Preparation 29, Chapter 4.

In Tables 6–17 and 6–18, the activities are compared in terms of the time required for the completion of the reduction.

Preparation of the precipitated nickel by the simplified method should involve a local reaction, accompanied by local heating, which, however, may be dissipated by the bulk of the liquid. Hence U–Ni–B(s) should resemble both the usual U–Ni–B and the usual U–Ni–CB. We immediately see from the tables that the activity of the former lies between those of the latter two catalysts.

Of all the catalysts, U–Ni–A is again the most active. U–Ni–A(s) shows some depression in activity, which, however, is almost negligible for practical purposes. It is worth noting that the crystallite size of U–Ni–A(s) (33–41 Å) is smaller than that of U–Ni–A (39–45 Å). Therefore, the activity of the catalyst may not be discussed solely from

the standpoint of its crystallite size, and we should allow for many different factors, in spite of the earlier discussion[13] which laid emphasis on the importance of crystallite size. When we compare like catalysts, as in Entry Nos. 29 and 210, a catalyst of smaller crystallite size is preferred, however (33 Å for the former, and 37 Å for the latter).

U–Ni–A(HCl), which is prepared by digesting precipitated nickel with hydrochloric acid, shows a somewhat lower activity. This may be due partly to the small nickel content of the catalyst and partly to the existence of some contaminating chlorine compound which remains unremoved on the surface of the catalyst.

U–Cu–C is included here to assure its efficacy in the reduction of carbonyl compounds.[34] The catalyst listed in the tables was prepared by the modified method (Preparation 29, Chapter 4).

6. 5. Selective and Partial Reductions

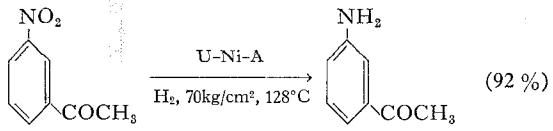
The Urushibara catalysts consist of a variety of modifications, each of which has its own characteristics and shows activity to varying degrees, according to the method of preparation. For example, we already know that U–Ni–B and U–Ni–NH_3 contain very small amounts of caustic alkali or ammonia even after washing, and favor alkaline reductions, whereas U–Ni–A is free from any alkali and favors reductions upon which the presence of alkali has an ill effect. The reduction of nitro compounds can be accomplished in the presence of U–Ni–A, whereas U–Ni–B must be thoroughly washed to remove any trace of alkali for the purpose of reducing nitro compounds. On the contrary, the reduction of carbonyl compounds is advantageous in the presence of U–Ni–B, whereas U–Ni–A is only effective when a small amount of alkali is added. However, ethylenic compounds are easily hydrogenated in the presence of either catalyst.

The above situation enables selective or partial reductions by the appropriate choice of catalyst or reaction conditions. The possibility of the selective reduction of nitro ketones or unsaturated ketones is self-evident.

Some diketones may undergo partial hydrogenation by virtue of the different rates of reduction of the two carbonyl groups. Also, some acetylenic compounds are effectively reduced to ethylenic compounds by the particular choice of a low activity catalyst.

6. 5. 1. Selective Reduction of Nitro Ketones

Reduction of nitro compounds is incomplete in the presence of alkali and gives diverse products. However, they are readily reduced to amino compounds in the presence of either U–Ni–A or U–Ni–B, provided the latter is warmed beforehand with saturated sodium chloride solution, followed by a thorough washing so that even a trace amount of alkali no longer remains on it (see Section 8. 1. 4). On the contrary, the effective reduction of carbonyl groups requires a small amount of alkali to be present. The situation is best utilized for the selective reduction of nitroacetophenone or its derivatives to the corresponding aminoacetophenones. An ethanol solution of *m*-nitroacetophenone easily gives *m*-aminoacetophenone, if it is reduced in the presence of U–Ni–A at pH 6–7 and under high pressure.[22]



(92 %)

The same reduction can also be carried out under atmospheric pressure.[18] Two moles of hydrogen are quickly absorbed when an ethanol solution of the substance is shaken with hydrogen at room temperature in the presence of U–Ni–B, previously treated with sodium chloride solution. The absorption rate falls at this stage and a second drop comes after another mole of hydrogen is absorbed, when reduction should be interrupted. The yield of *m*-aminoacetophenone is 90% of the theoretical (see Fig. 8–1).

Another example of the selective reduction of a nitro ketone is that of 3-nitro-4-methylacetophenone to 3-amino-4-methylacetophenone in the presence of U–Ni–A. For the conditions of such a high-pressure reduction, the reader is referred to Table 8–11.

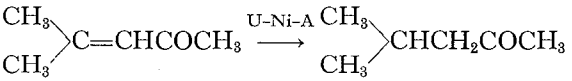
6. 5. 2. Selective Reduction of Unsaturated Ketones

Ethylenic compounds are easily hydrogenated in the presence of either U–Ni–A or U–Ni–B, under either atmospheric or higher pressures. Reduction proceeds at room temperature with the spontaneous elevation of temperature due to the heat of reaction. On the other hand, carbonyl compounds are not reduced quickly in the presence of U–Ni–A, which is free from alkali. Moreover, the rate of absorption of hydrogen is low at room temperature even in the presence of U–Ni–B and an abrupt rise in the rate comes only above 60°C.[14] This situation

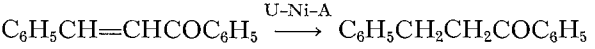
Table 6–19. Selective Reduction of Unsaturated Ketones in the Presence of U–Ni–A

Sample		Ni content of catalyst (g)	Solvent	Initial pressure (kg/cm²)	Temperature (°C)	Time (min)	Product	Yield (%)
Compound	Weight (g)							
mesityl oxide	50	0.5	ethanol	59	46–64	240	isobutyl methyl ketone	27
„	50	1	none	78	50–80	25	„	83
chalkone	115	10	ether	32	20	15	phenethyl phenyl ketone	92

renders possible the reduction of unsaturated ketones to saturated ketones by carrying out the reaction in the presence of neutral U–Ni–A, while keeping the temperature down so as to prevent the hydrogenation of the carbonyl group. Examples are provided by the high-pressure reduction of mesityl oxide and chalkone, for which the reaction conditions are shown in Table 6–19.



$$(CH_3)_2C{=}CHCOCH_3 \xrightarrow{\text{U-Ni-A}} (CH_3)_2CHCH_2COCH_3$$



$$C_6H_5CH{=}CHCOC_6H_5 \xrightarrow{\text{U-Ni-A}} C_6H_5CH_2CH_2COC_6H_5$$

Some comments must be added thereto. The reduction of mesityl oxide begins at 50°C, but the temperature rises spontaneously thereafter owing to the heat of reaction. The low yield of isobutyl-methyl ketone in the first row of Table 6–19 is due to the formation of an azeotropic mixture with the solvent ethanol. A better result is obtained when the reaction is carried out without any solvent.

6. 5. 3. Selective Reduction of Unsaturated Nitriles

Reduction of nitriles to amines is favored by the presence of a very small amount of alkali, hence U–Ni–B is preferred to U–Ni–A. A further investigation of this reduction has shown that U–Co–B is more active than U–Ni–B, with the formation of a lesser amount of secondary amine as a by-product,[8] just as Raney cobalt is more effective in this case than Raney nickel.*1) Ethylenic compounds, on the contrary,

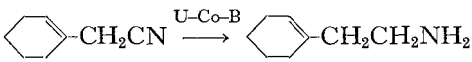
*1) W. Reeve and W. M. Eareckson, *J. Amer. Chem. Soc.*, **72**, 3299 (1950).

Table 6–20. Selective Reduction of Unsaturated Nitriles by Various Methods

Amount of nitrile, 10 g; Solvent, methanol 20 ml; Initial pressure, 90–100 kg/cm²; Temperature, 85–90°C; Cobalt content of catalysts, 0.5 g

Compound	U–Co–B		Raney Co		$LiAlH_4$	
	Yield (%)	m.p. of picrate (°C)	Yield (%)	m.p. of picrate (°C)	Yield (%)	m.p. of picrate (°C)
	80	168–172	82	167–171	65	168–172
	65	135–142	—	—	26	150–152
	80	160–165	81	161–165	66	169–170

are hydrogenated more effectively with nickel catalysts. One may well expect that unsaturated nitriles are reduced to unsaturated amines in the presence of U–Co–B, as it favors the reduction of nitrile groups over that of ethylenic bonds. In fact, this is best exemplified by the high-pressure hydrogenation of 1-cyclohexenylacetonitrile.[8]



The same reduction can be carried out in the presence of Raney cobalt or with lithium aluminum hydride. The melting point of the picrate of the product amine is the same in the above three reductions (Table 6–20), showing that the ethylenic bond is left entirely intact.

Somewhat different results are obtained for the reduction of cyclopentenyl- and cycloheptenyl-acetonitrile (Table 6–20). The melting points of the picrates of the products obtained with U–Co–B are considerably lower than those obtained with lithium aluminum hydride. This is also the case with Raney cobalt. This indicates that the catalytic reduction accompanies a partial hydrogenation of the ethylenic linkage and gives a considerable amount of saturated amine as a by-product. This is verified by the fact that only 60% (or 70%) of the calculated amount of hydrogen is absorbed when the hydrochloride of the product, cyclopentenylethylamine (or cycloheptenylethylamine), as it stands, is further hydrogenated in ethanol solution in the presence of a platinum oxide catalyst.

6. 5. 4. Partial Hydrogenation of Acetylenic Compounds

The partial hydrogenation of acetylenic to ethylenic compounds involves interruption of the reaction at a stage where just one mole of hydrogen has been absorbed. The possibility of such partial hydrogenation has attracted the interest of many workers, and many catalysts have been examined for use in this situation. At first, palladium was the most distinguished catalyst for this purpose because of its high selectivity. Later, Campbell and O'Connor*[1] found that Raney nickel also displays the same selectivity, and used it in the preparation of numerous olefins from the respective acetylenes. However, the selectivity of these catalysts is far from satisfactory, because their high activities are apt to bring about complete reduction; thus the end point of the absorption of just one mole of hydrogen must not be overlooked in order to achieve partial hydrogenation.

A trial to accomplish the partial hydrogenation of acetylenic compounds with Urushibara nickel has been made, following the example of the Raney nickel catalyst, but this turned out to be futile. To allow for the particular requirements of this reaction, a catalyst of intentionally low activity was prepared by treating precipitated nickel with 6–8% hydrochloric acid (U–Ni–A(HCl)). The reduction of phenylpropiolic acid was carried out in its presence and the reaction was interrupted after just one mole of hydrogen had been absorbed. The product was the expected *cis*-cinnamic acid, but the yield remained as low as 10–15%.

Of many publications which deal with attempts at partial hydrogenation, that of Paul and Hilly*[2] has been of greatest importance. They prepared Raney iron catalyst, which resembled Raney nickel in its preparation but turned out to have no capacity for hydrogenating ethylenic linkages. In its presence they succeeded in the partial hydrogenation of many acetylenic compounds. In view of their success, together with the apparent resemblance between Raney and Urushibara catalysts, an Urushibara iron catalyst was produced and used in the hydrogenation of 2-butyne-1,4-diol. The result was striking, and *cis*-2-butene-1,4-diol was obtained in a good yield.[22]

The next step was the improvement of this iron catalyst. There had been many contributions to the partial hydrogenation of 2-butyne-

*1) K. N. Campbell and M. J. O'Connor, *J. Amer. Chem. Soc.*, **61**, 2897 (1939).
*2) P. Paul and G. Hilly, *Bull. Soc. Chim. France*, [5] **6**, 218 (1939); A. F. Thompson and S. B. Wyatt, *J. Amer. Chem. Soc.*, **62**, 2555 (1940).

Table 6–21. Hydrogenation of 2-Butyne-1,4-diol in the Presence of Various Catalysts
Sample : 4.3 g of 2-butyne-1,4-diol (0.05 mole) in 50 ml of ethanol

Entry No.	Catalyst	Weight of catalyst[a] (g)		Initial pressure (kg/cm²)	Initial temperature (°C)	Working temperature (°C)	Time[b] (min)	Product
1	U–Fe(III)	2	(2.2)	51	23	23–105[c]	130	*cis*–2–butene–1,4–diol
2	U–Fe(II)	2	(4.6)	72.5	21	100–105	130	*cis*–2–butene–1,4–diol
3	U–Fe(III)–BA	2	(1.9)	50.5	28	105–118		none[d]
4[e]	U–Fe(III)	2	(0.65)	56	21	144–154	345	*cis*–2–butene–1,4–diol
5	U–Fe(III)–Ni	2.02[f]	(1)	70	21	101–105	60	*cis*–2–butene–1,4–diol
6	U–Fe(II)–Ni	2.02[f]	(5.3)	65	24	101–105	70	*cis*–2–butene–1,4–diol
7	U–Fe(III)–Co	2.05[g]	(1.6)	78	29	100–103	45	*cis*–2–butene–1,4–diol
8	U–Fe(II)–Co	2.05[g]	(5)	62.5	33	100–105	265	*cis*–2–butene–1,4–diol
9	U–Ni–A(s)(HCl)	0.5	(0.4)	58	24	24–36[h]	10	1,4–butanediol
10	U–Co–A(s)(HCl)	0.5	(0.6)	60	28	33–41[h]	50	*cis*–2–butene–1,4–diol
11	U–Co–B(s)	0.5	(3)	64	30	31–35[h]	70	*cis*–2–butene–1,4–diol

[a] Values before the parentheses are the weights of catalyst metals in the original chlorides. Those in the parentheses are the weights of catalysts, dried after the reaction.
[b] Duration of hydrogen uptake.
[c] Agitation was begun at room temperature and hydrogen uptake began at about 80°C. Reduction rate increased at about 100°C.
[d] Hydrogenation did not take place.
[e] 0.1 mole of the material in 50 ml of ethanol was reduced. Hydrogen was recharged four times.
[f] Fe 2 g and Ni 0.02 g.
[g] Fe 2 g and Co 0.05 g.
[h] A spontaneous rise of temperature was observed.

1,4-diol using Raney nickel,*1) palladium-calcium carbonate,*2) iron,*3) or partially poisoned copper, nickel, cobalt, and platinum catalysts.*4) Referring to these works, a full investigation was carried out in which the activities of the Urushibara iron catalysts, modified in various ways, were examined, and it was found that the most effective catalyst is an Urushibara iron to which a limited amount of nickel or cobalt has been added. Table 6–21 gives the details of the experiments, including results on some nickel and cobalt catalysts.

Hydrogenation was carried out in a 100 ml autoclave of the magnetic stirring type. The catalyst was first transferred carefully with ethanol into the autoclave and the air was completely replaced with hydrogen. The following conditions were employed: (1) sample: 2-butyne-1,4-diol (recrystallized from benzene, m.p. 58.5°C), 4.3 g (0.05 mole, except in the case of Entry No. 4 for which 0.1 mole was used); (2) solvent: ethanol (99%), 50 ml; (3) agitation frequency: 40–45 strokes per minute; (4) initial pressure: above 50 kg/cm^2. Agitation began as soon as the temperature reached the lower limit when the reaction began to take place. The range of the reaction temperatures is shown in the table. The pressure was measured every five minutes. When the reduction was over, the catalysts were filtered out and washed with ethanol. Most of the solvent was distilled off from the combined filtrate, and the residual liquid was distilled under reduced pressure. The product was *cis*-2-butene-1,4-diol, a colorless oil, b.p. 125–126°C/12 mmHg, yield 70–75%; except for the single case of the U–Ni–A(s)(HCl) catalyst, which gave a saturated product, 1,4-butanediol, a colorless oil, b.p. 131–132°/25 mmHg, yield 73%.

The first row (Entry No. 1) of Table 6–21 is a preliminary experiment intended to determine the temperature dependence of hydrogen uptake in the presence of a U–Fe(III) catalyst, establishing that the absorption of hydrogen begins at about 80°C and becomes marked above 100°C.

*1) A. Valette, *Ann. Chim.*, [12] **3**, 667 (1948); C. Prévost and A. Valette, *Compt. Rend.*, **222**, 327 (1946); N. Lozac'h, *Bull. Soc. Chim. France*, **1949**, 287; W. Reppe, *et al.*, *Ann.*, **596**, 44 (1955); J. Yasumura, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*) **82**, 281 (1961).

*2) A. W. Johnson, *J. Chem. Soc.*, **1946**, 1014; T. Fukuda and T. Kusama, *Bull. Chem. Soc. Japan*, **31**, 339 (1958).

*3) Badische Anilin -u. Soda-Fabrik, D.B.P. 873,545 (1941); *Chem. Zentr.*, **1953**, 7401; W. Reppe, *et al.*, *Ann.*, **596**, 43, 60 (1955).

*4) I. G. Farbenindustrie, German Pat. 734,312 (1938); German Pat. Org. Chem., 6,548; General Aniline and Film Corp., U.S. Pat. 2,300,598 (1939); *Chem. Abst.*, **37**, 2018 (1943).

Accordingly, a temperature of around 100°C was subsequently employed throughout. The second row (Entry No. 2) is a similar experiment with U–Fe(II), with a similar result, showing that there is little difference between the two catalysts. The behavior of U–Fe(III)–BA (Entry No. 3) was somewhat different from the expectation. Under similar conditions, it was completely inactive and no appreciable uptake of hydrogen was observed.

We have seen in the reduction of benzophenone that both a high reaction temperature and a high concentration of the substance to be reduced are particularly favorable for effective reduction.[34] In the fourth row of Table 6–21 (Entry No. 4), are shown the results of a reduction which was carried out at a higher temperature with twice the amount of 2-butyne-1,4-diol with a result which was far from satisfactory. It was suggested that the situation would be different if a greater amount of catalyst had been present.

The succeeding four runs are experiments with Urushibara iron catalysts modified by adding limited amounts of nickel or cobalt. It was found that in the reduction of acetophenone a better result could be obtained if the U–Ni–A was prepared from a nickel chloride solution to which a small amount of iron(III) chloride had been added, so that the catalyst contained a trace amount of iron, which acted as a promoter. Entry Nos. 5 and 6 are the corresponding modifications of an iron catalyst, where 1% of nickel was added to the iron. Both U–Fe(II)–Ni and U–Fe(III)–Ni prove, as expected, to have higher activities than would be displayed by the usual U–Fe(II) and U–Fe(III). The situation is different in the U–Fe–Co catalysts (Entry Nos. 7 and 8). The low activity of the cobalt catalyst itself enables the modified iron catalyst used for partial hydrogenation to contain a greater amount of cobalt (2.5%). With such a cobalt content, U–Fe(III)–Co shows a remarkably high activity, but the activity of U–Fe(II)–Co is unexpectedly low. This may be partly due to the low dispersability of the catalyst, but a full explanation can not be given as yet.

The last three experiments are intended to test the possibility of using catalysts other than iron, where a particularly low activity that would not bring hydrogenation to completeness is desired. These catalysts were prepared from precipitated metals obtained by a simplified method to give a somewhat lowered activity, and by treating them with an otherwise undesirable agent. The first of them (Entry No. 9) involves U–Ni–A(s)(HCl), which is a composite catalyst of U–Ni–A(s) and U–Ni–A(HCl) of lowered activity. The result shows,

contrary to expectation, that the composite catalyst is still active enough to give only a saturated product: 1,4-butanediol. The last two catalysts are U–Co–A(s)(HCl) and U–Co–B(s). Hydrogenation in the presence of either catalyst seems to be pomising, provided the reaction is interrupted when the rate of hydrogen uptake suddenly falls. This stage comes when just one mole of hydrogen has been absorbed.

In passing, it is to be noted that the absorption of hydrogen is not observed during the first 5 to 15 minutes after stirring is started at room temperature. When the temperature exceeds 31°C, absorption begins to take place and the temperature rises spontaneously owing to the heat of reaction. Room temperature being not far from the lower working temperature limit, it is not clear whether the first time lag is due to an induction period or to too low a starting temperature.

6. 5. 5. Partial Hydrogenation of α-Diketones

The reduction of benzil to hydrobenzoin in the presence of various Urushibara nickel catalysts[37] has already been mentioned and summarized in Table 6–18. The absorption of hydrogen occurs in two steps; there is a sudden fall in hydrogen uptake between the two steps, which lasts for a short time. The two values in parentheses in Table 6–18 refer to the first and second absorption periods, respectively. A typical example is shown in Fig. 6–13. The sudden change in rate

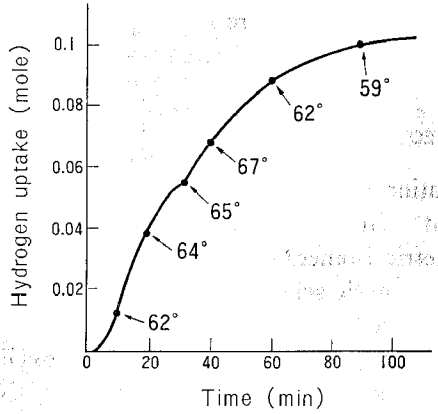


Fig. 6–13. Hydrogen Absorption Curve of Benzil

Benzil: 0.05 mole (10.5 g)
Catalyst: U–Ni–CB (Ni 0.5 g)
Solvent: ethanol 40 ml
Initial pressure: 101 kg/cm²

Table 6–22. Partial Reduction of α-Diketones in the Presence of U–Ni–A

Sample	Solvent	Catalyst[a]	Initial pressure (kg/cm²)	Temperature (°C)	Time (min)	Product	Yield (%)
benzil 10.5 g (0.05 mole)	ethanol (50 ml)	U–Ni–A	80	20	100	benzoin	76
benzil 10.5 g (0.05 mole)	ethanol (50 ml)	U–Ni–A(s)	85	22	115	benzoin	80
furil 9.5 g (0.05 mole)	ethanol (100 ml)	U–Ni–A	56	60–63	90	furoin	81
furil 9.5 g (0.05 mole)	ethanol (100 ml)	U–Ni–A(s)	60	60–62	100	furoin	79

[a] Containing 0.5 g of Ni; 0.5 ml of 5% NaOH was added.

is regarded as an indication of the completion of the hydrogenation of one of the two carbonyl groups in the α-diketone, because just one mole of hydrogen is absorbed at this stage. We can expect that the partial hydrogenation of α-diketone to α-hydroxy ketone can be attained if we constantly watch the rate or amount of hydrogen uptake, and interrupt the reaction at a stage when just one mole of hydrogen has been absorbed, or when the absorption rate falls off suddenly.

This was realized in the reduction of benzil and furil, the results of which are summarized in Table 6–22. As furil is only sparingly soluble in ethanol at room temperature, experiments on this material were carried out at a higher temperature in the presence of a larger amount of solvent.

6.6. Steric Selectivity

The hydrogenation of olefins is effected in the presence of Urushibara nickel catalyst. An interesting suggestion was given by the hydrogenation of geometric isomers of oleic acid; namely, that the catalyst was likely to display steric selectivity. A series of experiments on this subject followed immediately, which involved the reduction of geometric isomers of a number of unsaturated carboxylic acids or their derivatives in the presence of either U–Ni–A or U–Ni–B, under high or ordinary pressures.

The first experiment was the high-pressure hydrogenation of two pairs of unsaturated acids, *i.e.*, maleic and fumaric acids and citraconic and mesaconic acids, under the same conditions in the presence of each catalyst. The reduction times are listed in Table 6–23, which clearly

Table 6–23. High-pressure Hydrogenation of Stereoisomeric Olefins in the Presence of Various U–Ni Catalysts

Compound	Weight of sample (g)	Catalyst	Ni content of catalyst (g)	Solvent	Medium	Initial pressure (kg/cm²)	Temperature (°C)	Time (min)	Product
diethyl maleate	16	U–Ni–A	0.5	ethanol	neutral	60	29	4.5–5	diethyl succinate
diethyl fumarate	"	"	"	"	"	"	"	5	"
diethyl maleate	10	U–Ni–A	0.5	ethanol	neutral	39	32	3.5–4	"
diethyl fumarate	"	"	"	"	"	"	"	3.5	"
diethyl maleate	16	U–Ni–B	0.5	ethanol	weak alkaline	49	32	5–6	"
diethyl fumarate	"	"	"	"	"	"	34	5.5–6.5	"
diethyl citraconate	9.3	U–Ni–A	0.5	ethanol	neutral	35	30	30	diethyl methylsuccinate
diethyl mesaconate	"	"	"	"	"	"	31	80	"
sodium citraconate	13	U–Ni–A	1.0	water	neutral	41	33	30	sodium methylsuccinate
sodium mesaconate	"	"	"	"	"	"	34	50	"
sodium citraconate	10	U–Ni–A	0.5	water	neutral	44	20	30	"
sodium mesaconate	"	"	"	"	"	"	18	110	"

Table 6–24. Hydrogenation of Stereoisomeric Olefins under Atmospheric Pressure in the Presence of U–Ni–A

Compound	Amount of sample		Ni content of catalyst (g)	Solvent	Temperature (°C)	Time (min)	Rate of H_2 uptake (ml/min)	Volume of absorbed H_2 (ml)		Product
	mole	g						calc.	obs.	
diethyl maleate	0.015	2.578	0.25	ethanol	23	16–17		336	337	diethyl succinate
diethyl fumarate	„	2.576	„	„	„	17–18		„	336	„
sodium maleate	0.01	1.16	0.25	water	26	17		224	225	sodium succinate
sodium fumarate	„	„	„	„	„	16–17		„	225	„
sodium maleate	0.01	1.16	0.05	water	20–23	40		224	220	„
sodium fumarate	„	„	„	„	„	60–70		„	222	„
diethyl citraconate	0.015	2.79	0.5	ethanol	25		330/105	336	332	diethyl methylsuccinate
diethyl mesaconate	„	„	„	„	„		147/105	„	336	„
oleic acid	0.0036	1.005	1.0	ethanol	20		60/150	82	70	stearic acid
elaidic acid	„	1.004	„	„	21		34/165	„	82	„
oleic acid	0.0036	1.000	1.0	ethanol	19		70/140	82	86	„
elaidic acid	„	„	„	„	„		40/185	„	81	„
sodium *cis*–cinnamate	0.0034	0.507	0.25	water	24	6–7		77	78	sodium hydrocinnamate
sodium cinnamate	„	„	„	„	„	„		„	78	„
sodium *cis*–cinnamate	0.0045	0.670	0.25	water	19	8		101	104	„
sodium cinnamate	„	„	„	„	20	7–8		„	105	„
sodium *cis*–cinnamate	0.0047	0.700	0.05	water	19	40		106	121	„
sodium cinnamate	„	„	„	„	„	45		„	106	„

shows that the ester or salt of citraconic acid is more susceptible to hydrogenation than its stereoisomer, mesaconic acid; but the difference in the reaction rate is almost imperceptible between maleic and fumaric acid.

In another experiment which followed, allowance was made for the mild conditions appropriate for bringing about steric selectivity by carrying out the hydrogenation under ordinary pressure in the presence of U–Ni–A (Table 6–24). It was found that sodium maleate was more readily hydrogenated than sodium fumarate, when the amount of the catalyst was small, although the situation was the same as in the high-pressure hydrogenation when the amount of catalyst used was large. Exactly the same trend was observed with the pair, cinnamic and *cis*-cinnamic acids. The rate of hydrogenation of diethyl citraconate was always higher than that of diethyl mesaconate. The same is also the case for the pair, oleic and elaidic acid.

In sum, Urushibara nickel catalysts have steric selectivity to some degree for pairs of *cis-trans* isomers, and *cis* compounds are in general more susceptible to hydrogenation than their corresponding *trans* compounds. The difference, however, is only discernible when the amount of catalyst used is small.

6.7. Solvent Effect

A solvent effect often plays a significant role in liquid-phase catalytic reduction. The subject has been investigated by many authors, particularly by D. V. Sokol'skii,*[1] who has discussed the effect of solvent on the basis of kinetic theory. Orito and Kawachi[33] studied the effect of solvent on the reduction of acetone in the presence of Ni–Cr_2O_3–kieselguhr and showed that such solvents as hydrocarbons (*n*-heptane, cyclohexane), secondary and tertiary alcohols (isopropyl alcohol, *tert*-butyl alcohol), isopropyl ether, or water expedite the reduction; whereas solvents such as primary alcohols (methyl alcohol, ethyl alcohol), ethyl ether, or dioxane tend to suppress activity.

It is widely recognized that a solvent containing oxygen atoms often acts as a catalyst poison, because of the high susceptibility of the oxygen atom to adsorption. In general, this is not the case for an oxygen atom adjacent to a secondary or tertiary carbon atom, conceivably because steric disposition is unfavorable for adsorption. The effect of

*1) D. V. Sokol'skiĭ, *Chem. Abst.*, **55**, 15076 (1961).

solvent is particularly remarkable in the ring hydrogenation of benzene or toluene; hydrocarbons are good solvents for rapid hydrogenation, but solvents containing oxygen atoms, particularly primary alcohols and dioxane, strongly restrain hydrogenation.

Such a solvent effect is also often encountered with Raney nickel or Urushibara nickel, and the same authors noted that the same tendency for a solvent to show promotive or suppressive action is observed for every catalyst.

Information is available regarding the effect of solvent on the reduction of acetone, benzene, toluene, and cumene in the presence of U–Ni–A prepared by a standard method (Preparation 4, Chapter 4).

(*a*) *Reduction of Acetone*[33]

U–Ni–A (Ni content 0.5 g) was washed four times by successive decantation with the solvent to be used in the reduction, thus replacing the water with solvent. When the solvent was immiscible with water, as in the case of *n*-heptane, the catalyst was first washed with isopropyl alcohol by the above process and then with the solvent specified. Table 6–25 shows the rate of hydrogen uptake in the reduction of acetone under an ordinary pressure in the presence of the above catalyst. We can easily verify that reduction readily takes place in hydrocarbons, but is slow in other solvents, such as water or alcohols.

Table 6–25. Ordinary Pressure Reduction of Acetone in Various Solvents in the Presence of U–Ni–A

Acetone, 5 ml; Solvent, 20 ml; Ni content of the catalyst, 0.5 g; Temperature, 25°C

Solvent	Rate of H_2 uptake (ml/min)
n-heptane	12.6
methylcyclohexane	12.1
n-hexane	9.2
cyclohexane	9.0
methyl alcohol	1.6
ethyl alcohol	1.2
isopropyl alcohol	2.2
sec-butyl alcohol	1.3
water	2.4

(b) Hydrogenation of Benzene, Toluene, and Cumene

Aromatic hydrocarbons are, in general, not hydrogenated in the presence of U–Ni–A under ordinary conditions.[31] This catalyst, however, turned out to retain the ability to hydrogenate benzene rings if the reaction were carried out in hydrocarbon solvents, free from even trace amounts of water.[40] We shall present the results of an experiment which uncovered this kind of activity.

To accomplish the complete replacement of solvent, the catalyst was separated from the solvent by means of centrifuging instead of decantation. U–Ni–A (containing 1 g of nickel) prepared from aqueous solution was transferred to a 50 ml centrifuge tube and washed by centrifuging 5 times with water, 5 times with isopropyl alcohol, and then 5 times with the solvent specified (or with the material to be reduced itself, in the case of a solvent-free reduction.) The second process was omitted when the solvent was miscible with water.

The finished U–Ni–A was placed in a 200 ml autoclave of the magnetic stirring type together with a definite amount of benzene, toluene, or cumene, and hydrogenation was continued under hydrogen pressure from 40 to 20 kg/cm^2 with agitation at 120 strokes/min. Table 6–26 shows the initial rate of hydrogen absorption, which refers

Table 6–26. High-pressure Hydrogenation of Aromatic Hydrocarbons in Various Solvents in the Presence of U–Ni–A

Ni content of the catalyst, 1 g; Solvent, 30 ml

	Benzene 15 ml (0.169 mole)	Toluene 15 ml (0.141 mole)	Cumene 45 ml (0.323 mole)
Solvent \ Temperature	110°C	135°C	155°C
none	326	231	620
n–hexane	192	—	—
n–heptane	220	139	176
cyclohexane	188	—	—
methylcyclohexane	216	137	220
sec–butyl alcohol	2	0	0
isopropyl alcohol	0	—	—
ethyl alcohol	0	—	—
isopropyl ether	18	—	—
dioxane	0	—	—

Values in the table refer to the initial rates of hydrogen uptake (ml/min).

to the time required for the pressure to fall from 40 kg/cm² to 30 kg/cm², except for cases where the absorption rate is extremely low.

In 30 ml of cyclohexane, 15 ml of benzene (13.2 g, 0.169 mole) absorbed almost a quantitative amount of hydrogen at 80–120°C in 120 minutes. With 15 ml of toluene (13.0 g, 0.141 mole) in 30 ml of methylcyclohexane at 130–140°C, or 45 ml of cumene (39.0 g, 0.323 mole) without solvent at 155°C, the quantitative absorption of hydrogen was again observed; the reduction times were 80 and 145 minutes, respectively. In every case, the reaction stopped when the theoretical amount of hydrogen was absorbed, and the product was the corresponding alicyclic hydrocarbon in an almost quantitative yield.

Hydrogenation in alcohols or ethers, on the contrary, either did not take place or proceeded only at an extremely low rate.

Thus, it has been found that aromatic compounds are hydrogenated to alicyclic compounds in a hydrocarbon solvent or in the absence of any solvent, provided the catalyst is completely free from water. However, Urushibara catalysts can not compare with Raney nickel in this respect, as the latter is known to be far more active in the same reduction.

It must be kept in mind that alcohol is a poisonous substance in the catalytic hydrogenation of aromatic compounds and, in particular, even a very small amount of ethyl alcohol may largely suppress the activity toward ring hydrogenation, because we are accustomed to the convention in which we frequently treat Raney or Urushibara catalysts with ethanol after washing with water.

U–Ni–B also shows the same activity to a comparable extent provided the above process is preceded by washing with water many times until the wash water is completely neutral to phenolphthalein. The washing process, however, is very troublesome (it should be repeated 30 times or more at room temperature even if it is effected by centrifuging), so that the use of U–Ni–B is not recommended for this purpose.

7. Vapor-phase Hydrogenation

Sabatier's apparatus is a typical device for vapor-phase hydrogenation on a laboratory scale. Ever since Sabatier invented a method of reduction using an apparatus of this kind in 1897, a great number of modifications and improvements have been attempted. The method is now widely applied, not only to the hydrogenation of gaseous material, but to the hydrogenation of liquid or solid material as well. In the latter cases the materials are vaporized and placed together with hydrogen over a catalyst in a reaction tube.

Sabatier's method originally consisted of using "reduced nickel" as a catalyst for hydrogenation. The reaction tube is filled with nickel oxide, usually supported on a suitable carrier, such as kieselguhr, silica gel, pumice stone, etc. The oxide is reduced with hydrogen to catalytically active nickel metal, over which the vapor of the sample, mixed with hydrogen, is then allowed to pass. Cobalt, copper, and iron are also used as catalysts. A nickel-copper combination has proved very effective.

The use of an Urushibara nickel catalyst for vapor-phase reduction has been investigated. Its success, no doubt, has been worth waiting for, as the catalyst can be very easily prepared. However, some difficulties have been encountered. In Sabatier's method, the catalyst is automatically protected from contact with the air, as it is prepared from dried nickel oxide in the reaction tube in a hydrogen gas flow. On the contrary, Urushibara nickel catalyst must be transferred to the reaction tube from the vessel in which it is prepared. The catalyst is wet when it is prepared and always loses its activity if dried in air. In particular, active U–Ni–A ignites spontaneously when dried in air. Hence, it is necessary to fill the tube with the catalyst while the latter is still wet, and to dry it in a hydrogen gas flow, air being excluded as completely as possible. With Sabatier's apparatus, the process is very troublesome and in some cases even impossible. New apparatus and a particular catalyst have therefore devised for the purpose, and are presented in the following.

7.1. Vapor-phase Hydrogenation in a U-tube Apparatus

A specially designed apparatus has been devised[15] for the purpose of applying U–Ni–A to vapor-phase reduction (Fig. 7–1).

The apparatus consists of a U–tube, 3 cm in diameter and about 50 cm long, made of hard glass. About 3/4 of the tube is filled with granulated pumice which has been purified beforehand by heating with concentrated hydrochloric acid to dissolve away any soluble matter. One end of the tube is filled with glass wool to support the pumice grains.

U–Ni–A is freshly prepared according to Preparation 4, Chapter 4, and is washed well with water aud then with ethanol to replace the water. Most of the ethanol is decanted, and the catalyst, suspended in the remaining ethanol, is poured together with the solvent onto the pumice stone in the U-tube. The catalyst settles on the pumice stone as it flows through the tube. The tube is tilted towards the glass-wool-filled end to allow the catalyst to penetrate to the lower end and to spread over the whole surface of the grains of pumice. The tube is then refilled with a supplemental amount of new pumice stone, and the remaining ethanol is decanted. The end of the U-

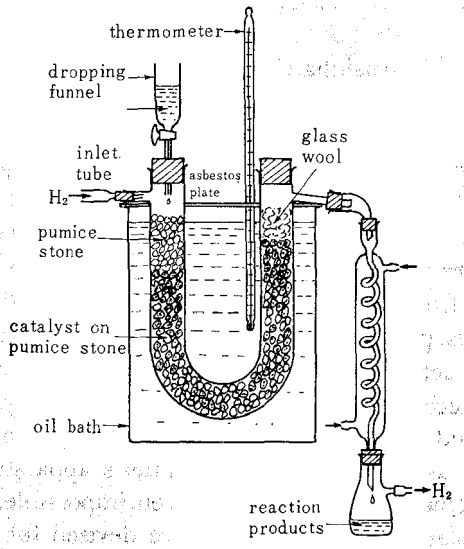


Fig. 7–1. Apparatus for Hydrogenation

tube which has no glass wool is fitted with a small dropping funnel, from which the sample liquid is to be added onto the pumice stone. A side tube underneath serves as the hydrogen inlet.

The other end of the U-tube is stoppered, and the side tube is fitted with a condenser which connects with a receiver for collecting the product. The end of the apparatus may also be connected with a receiver containing some absorbing agent, or with a dry ice trap when it is required to collect gaseous products. The U-tube is placed in an oil bath.

The procedure of reduction with this apparatus is as follows: The oil bath is heated to the boiling point of ethanol and hydrogen is passed through to remove the solvent in the form of vapor. The receiver is then replaced by one for collecting the product, and the temperature is raised. When the proper temperature is reached, the liquid sample is added dropwise from the dropping funnel into the tube. The liquid is vaporized on the hot pumice stone and is allowed to pass together with hydrogen gas onto the catalyst surface, where it is hydrogenated. The product is then carried to the condenser by the hydrogen, cooled to a liquid, and collected in the receiver. To carry out hydrogenation effectively, the addition of the sample should be as slow as possible, so that it can be mixed with a sufficient amount of hydrogen.

The flow of hydrogen is continued for a further 30–60 minutes at the temperature specified to complete hydrogenation and, at the same time, to expel the product. When the reaction is over, the product collected in the receiver is fractionated and identified.

U–Ni–A: Table 7–1 illustrates several results obtained in this way with U–Ni–A.[15] Nitrobenzene was reduced to aniline in good yield, and styrene and acetophenone were easily reduced to ethylbenzene. The results for benzene and benzonitrile were somewhat different from those expected. With Sabatier's reduced nickel, the former is readily reduced to cyclohexane,*1) and the latter gives toluene and ammonia almost in quantitative yields.*2) In the presence of U–Ni–A, on the other hand, benzene withstands hydrogenation and benzonitrile gives mostly primary and secondary amines together with a lesser amount of toluene.

U–Ni–BA: We already know that U–Ni–BA is a catalyst whose ac-

*1) P. Sabatier and J. B. Senderens, *Compt. Rend.*, **132**, 210 (1901).

*2) P. Sabatier and J. B. Senderens, *ibid.*, **140**, 482 (1905); K. Hata, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **23**, 224 (1944); M. Tanaka, K. Watanabe, and K. Hata, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Section*), **76**, 1392 (1955).

Table 7–1. Vapor-phase Hydrogenation of Aromatic Compounds in the Presence of U–Ni–A

Compound	Weight of sample (g)	Weight of nickel (g)	Temperature (°C)	Time (hr)	Flow rate of sample (g/min)	Weight of product (g)	Product and yield (%)
nitrobenzene	10	4	220	3	0.08	9.7	aniline (81)
benzene	10	4	180	4	0.06	9.0	(benzene, recovered)
styrene	10.4	4	165	3	0.08	9.3	ethylbenzene (88)
acetophenone	9.9	4	200	3 ½	0.06	9.1	ethylbenzene (90)
benzonitrile	8.0	4	250	3	0.07	6.5	toluene (14) benzylamine (29) dibenzylamine (41) ammonia (50)

Table 7–2. Vapor-phase Hydrogenation of Aromatic Compounds in the Presence of U–Ni–BA

Compound	Weight of sample (g)	Weight of nickel (g)	Temperature (°C)	Time (hr)	Flow rate of sample (g/min)	Product and yield (%)
nitrobenzene	8	1	240	5	0.038	aniline[a] (58)
phenol	10	4	185	6	0.034	cyclohexanol (79)
styrene	4.3	1	195	4	0.029	ethylbenzene (91)

[a] Besides aniline, high molecular amines were obtained as by-products.

tivity is comparable to that of the ordinary Urushibara nickel catalyst in liquid-phase reduction, and that it is especially favorable for the hydrogenation of benzene rings.[20]

Effort has been made to apply the particular activity of this catalyst to vapor-phase reduction.[26] The preparation of U–Ni–BA followed Preparation 14, Chapter 4, where the precipitated nickel is produced using commercial aluminum powder (ca. 200 mesh). To effect the ion-exchange reaction, a detergent was added to suppress frothing which, otherwise, would carry aluminum powder to the surface of the solution. The catalyst obtained by digesting the precipitated nickel with 20% sodium hydroxide solution showed a somewhat lower activity in liquid-phase reduction, but exhibited sufficient activity in vapor-phase reduction. The catalyst is a fine black powder, so that reduction is best carried out in the U-tube apparatus with pumice stone as the carrier.

Several examples are given in Table 7–2.

7.2. Vapor-phase Hydrogenation with Sabatier's Apparatus

We have seen thus far that ordinary U–Ni–A or U–Ni–BA can be used in vapor-phase reduction in place of Sabatier's reduced nickel catalyst. However, the catalyst suffers from the disadvantage that it requires a particular device, such as the U-tube apparatus, and that the filling of the tube with the catalyst is somewhat troublesome. Moreover, both U–Ni–BA from commercially available aluminum powder and U–Ni–A prepared by the standard method are fine powders, and are apt to lose their activities while being charged into the tube in a semi-dry state.

An attempt has been made to improve U–Ni–BA by preparing the precipitated nickel with coarse grains of aluminum (45 mesh) instead of aluminum powder; the precipitated nickel was then treated with 20% sodium hydroxide solution. The product was washed with water and then with ethanol to replace the water. The wet catalyst was mixed with purified kieselguhr "Hyflosupercel" and the mixture was placed in the reaction tube of an ordinary Sabatier's apparatus while still half-wet. With this reaction tube, the reduction of acetophenone give ethylbenzene in good yield.

The method was further modified, and U–Ni–AA was established as a most profitable catalyst for vapor-phase reduction.[26]

The precipitated nickel is prepared from nickel chloride solution

Table 7–3. Vapor-phase Hydrogenation of Aromatic Compounds

Catalyst	Compound	Weight of sample (g)	Weight of nickel (g)
U–Ni–BA[a]	acetophenone	5	3
U–Ni–AA	nitrobenzene	5	8
U–Ni–AA	phenol	5	8
U–Ni–AA	benzonitrile	5	8
U–Ni–AA	benzene	5	8
U–Ni–AA	styrene	5	8
U–Ni–AA	acetophenone	5	8

[a] The catalyst was prepared from aluminum grains of 45 mesh. It was supported on "Hyflosupercel" as a carrier.

and aluminum grains (45 mesh), and treated with acetic acid. As aluminum hardly reacts with acetic acid alone, a supplementary device, such as the addition of an inorganic salt, is necessary. The treatment requires both a high concentration (40%) of acetic acid saturated with sodium chloride, and a high digestion temperature (70°C). The details of preparation are described in Preparation 18, Chapter 4. Nickel, deposited on the surface of aluminum grains, will not separate from the latter when it is treated with acetic acid, and thus protects the latter from dissolving. Aluminum grains, remaining undissolved after digestion is complete, act as a carrier for the catalyst. The U–Ni–AA is therefore a granular catalyst, a combination of catalyst and carrier, so that it can be charged in a semi-dry state into the tube without any difficulty.

With U–Ni–AA, the following reduction scheme is now available: Reduction is carried out in Sabatier's apparatus, equipped with a hard glass tube 1.8 cm in diameter and 90 cm in length, which is somewhat tilted and heated in an electric furnace. The catalyst is put into the reaction tube and heated to the specified reaction temperature, while the methanol used for washing the catalyst is completely expelled from the tube. The vaporized sample is then introduced, together with a large excess of hydrogen, onto the catalyst, where it is hydrogenated. The product is carried to the condenser and collected in a receiver. It is purified by fractionation.

Several results are given in Table 7–3. Comparing with Table 7–1 and 7–2, we immediately find several interesting points.

With U–Ni–AA, benzene rings are easily reduced to cyclohexane

in the Presence of Either U–Ni–BA or U–Ni–AA

Temperature (°C)	Time (hr)	Flow rate of sample (g/min)	Product and yield (%)
200	1 ¾	0.114	ethylbenzene (52)
230	2	0.094	aniline[b] (65)
180	3 ½	0.111	cyclohexanol (66)
250	2	0.075	toluene (76)
176	2 ⅓	0.046	cyclohexane (83)
150	2	0.073	ethylcyclohexane (71)
190	2	0.069	ethylcyclohexane (71)

[b] Besides aniline, high molecular amines were obtained as by-products.

rings, except for a limited number of cases, such as those of nitrobenzene and benzonitrile; whereas the reduction is effected by U–Ni–BA only in the single case of phenol, and never occurs in the presence of U–Ni–A. For instance, styrene and acetophenone are reduced to ethylbenzene by U–Ni–BA, but they give ethylcyclohexane in the presence of U–Ni–AA. Phenol gives cyclohexanol, and nitrobenzene gives aniline in the presence of either catalyst, but benzene is reduced to cyclohexane only by the latter. It is apparent that U–Ni–AA is the only catalyst which effectively hydrogenates aromatic rings. Hence, this catalyst is most profitable for vapor-phase hydrogenation both because of the high activity which it exhibits in many reductions, and because of the ease with which it is handled. Note that the reduction of benzonitrile in its presence gives toluene in a good yield, in contrast to the case of U–Ni–A (Table 7–1).

8. Applications

In regard to catalytic activity, Urushibara nickel is very similar to Raney nickel in many respects. It can replace the latter in almost every reduction, and gives products in almost the same yields.

Urushibara nickel catalysts, just like Raney nickel, are most utilized in hydrogenation and reduction, but can also be used in dehydrogenation and reductive desulfurization, and sometimes in reductive alkylation, reductive condensation, hydration, etc.

8. 1. Hydrogenation and Hydrogenolysis

Urushibara nickel catalysts are usually employed in liquid-phase hydrogenation under either ordinary or high pressures, but can be used as well in vapor-phase reduction. In liquid-phase reduction, the customary apparatus may be used without any modifications. For instance, reduction under ordinary pressure can make use of the apparatus previously in use, which consists of a reactor capable of strong shaking, combined with a reservoir of hydrogen and a measuring gas buret. Reduction under high pressure is effected in various shaking or stirring autoclaves. For the laboratory, a vertical autoclave of 200–500 ml capacity, provided with a magnetic stirrer, is most convenient.

The Urushibara nickel catalysts can be used in vapor-phase reduction. This is best accomplished with U–Ni–AA, which allows the use of ordinary apparatus. Catalysts such as U–Ni–A require particular devices and, what is worse, are not so effective (see Chapter 7).

8. 1. 1. Hydrogenation of Ethylenic and Acetylenic Compounds

Unsaturated compounds having double or triple bonds are easily hydrogenated to the corresponding saturated compounds in the presence of Urushibara nickel catalysts. The reactions are effected by liquid-phase hydrogenation under either ordinary or high pressures. Vapor-phase hydrogenation can also be applied for the same purpose, in which case the use of U–Ni–AA is preferred. In liquid-phase hydrogenation, the solution remains neutral if U–Ni–A is used, and be-

Table 8–1. Hydrogenation of Ethylenic and Acetylenic Compounds under Atmospheric Pressure

Compound	Amount of sample		Catalyst	Nickel content[b] (g)	Solvent	Temperature (C°)	Time (min)	Product	Reference
	mole	g							
sodium cinnamate	0.02	3.40	U-Ni-B	0.5	water 50 ml	25	16	sodium hydrocinnamate	18)
ethyl cinnamate	0.02	3.52	„	0.5	ethanol 20 ml	25	4	ethyl hydrocinnamate	18)
„	0.02	3.52	U-Ni-A	0.4	„	25	8	„	
„	0.02	3.52	U-Ni-A[a]	0.4	„	25	6	„	
sodium cinnamate	0.0045	0.67	U-Ni-A	0.25	water	20	7–8	sodium hydrocinnamate	
sodium *cis*-cinnamate	0.0045	0.67	„	0.25	„	19	8	„	
sodium maleate	0.01	1.16	„	0.25	„	26	17	sodium succinate	
sodium fumarate	0.01	1.16	„	0.25	„	26	16–17	„	
diethyl maleate	0.015	2.576	„	0.25	ethanol	23	16–17	diethyl succinate	
diethyl fumarate	0.015	2.578	„	0.25	„	23	17–18	„	
diethyl citraconate	0.015	2.79	„	0.5	„	25	—	diethyl methylsuccinate	
diethyl mesaconate	0.015	2.79	„	0.5	„	25	—	„	
oleic acid	0.0036	1.00	„	1.0	„	19	—	stearic acid	
elaidic acid	0.0036	1.00	„	1.0	„	19	—	„	
propargyl alcohol	0.01	0.561	U-Ni-B	0.5	„	25	50	propyl alcohol	18)

[a] Prepared by treatment with propionic acid.

[b] Weight of nickel in the original nickel chloride is to be understood. True weight in the catalyst is somewhat smaller.

Table 8–2. Hydrogenation of Ethylenic and

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent
	mole	g			
styrene	0.5	52	U-Ni-B	1	ether
„	1.96	200	„	1	none
„	1	104	U-Ni-A	1	none
stilbene	0.03	4.7	U-Ni-A[a]	1	ethanol
crotonic acid	0.10	8.6	U-Ni-B	1	„
oleic acid	0.16	45.6	U-Ni-B	2	„
„	0.10	28.0	U-Ni-A	1	„
cinnamic acid	0.02	2.5	U-Ni-B	2	„
ethyl cinnamate	0.06	10.1	„	1	„
diethyl maleate	0.95	16.0	U-Ni-A	0.5	„
diethyl fumarate	0.95	16.0	„	0.5	„
diethyl citraconate	0.05	9.3	„	0.5	„
diethyl mesaconate	0.05	9.3	„	0.5	„
mesityl oxide	0.5	49.07	„	0.5	„
„	0.5	49.07	„	1	none
chalkone	0.54	112	„	10	ether
tolan	0.02	3.6	U-Ni-A[a]	1	ethanol
„	0.02	4.0	U-Ni-A[b]	2	„
2-butyne-1,4-diol	0.05	4.3	U-Ni-A(s)(HCl)	0.5	„
„	0.05	4.3	U-Fe(III)	Fe 2	„
„	0.05	4.3	U-Fe(II)	Fe 2	„
„	0.05	4.3	U-Co-A(s)(HCl)	Co 0.5	„

[a] Prepared from nickel chloride with added copper sulfate (0.16 g Cu)

[b] The precipitated nickel was prepared from 9.5 g of nickel sulfate and zinc dust. It was treated with acetic acid to give the catalyst.

comes weakly alkaline if U–Ni–B is employed; but this does not affect the result of hydrogenation.

Most unsaturated compounds are easily hydrogenated at room temperature and under ordinary pressure, but high pressure hydrogenation is preferable for large scale operations. Usually, high pressure hydrogenation readily proceeds at ordinary temperatures, and a spontaneous rise in temperature is often observed on account of the heat of reaction, as in the hydrogenation of large amounts of styrene in the absence of any solvent. It sometimes happens that sterically hindered unsaturated compounds absorb hydrogen only at higher temperatures. The ethyl-

Acetylenic Compounds under High Pressure

Initial pressure (kg/cm^2)	Temperature[c] (°C)	Time (min)	Product	Yield (%)	Reference
49	20	360	ethylbenzene	—	21)
94	18→32	60	„	85	23)
80	19→56	20	„	90	21)
49	20–21	60	bibenzyl	87	21), 22)
57	15–16	60	butyric acid	>60	23)
57	40–100	60	stearic acid	80	23)
68	60–114	90	„	82	21), 22)
51	20	90	hydrocinnamic acid	—	23)
69	26	15	ethyl hydrocinnamate	86	
60	29	5	diethyl succinate	—	
60	29	5	„	—	
35	30	30	diethyl methylsuccinate	—	
35	31	80	„	—	
59	46–64	240	4-methyl-2-pentanone	27	
78	50→80	25	„	83	
32	20	15	1,3-diphenyl-1-propanone	92	
49	20–21	60	bibenzyl	87	
37	23–24	15	„	91	
58	24→36	10	1,4-butanediol	73	38)
51	100–105	130	*cis*-2-butene-1,4-diol	75	38)
72	100–105	130	„	75	38)
60	33→41	50	„	75	38)

[c] An arrow (→) indicates a spontaneous rise of temperature.

enic bond of cholesterol can not be hydrogenated in an ethanol solution.

Examples of liquid-phase hydrogenation, either under ordinary pressure or under high pressure, are given in Tables 8–1 and 8–2. We have noted many interesting points, which are discussed below.

The hydrogenation of cinnamic acid in ethanol proceeds very slowly under ordinary pressure, so that the hydrogenation of 0.02 mole of this compound requires as much as 40 minutes. When the acid is converted to its sodium salt, its hydrogenation in aqueous solution occurs in 16 minutes. Hydrogenation of the ethyl ester of the same acid requires only 4 minutes. A free carboxyl group may act as a kind of poision.

Table 8–3. Vapor-phase Hydrogenation

Compound	Weight of sample (g)	Catalyst	Nickel content (g)	Temperature (°C)
styrene	10.4	U–Ni–A	4	165
„	4.3	U–Ni–BA	1	195
„	5	U–Ni–AA	8	150

The hydrogenation of oleic acid proceeds very slowly at room temperature. Eeven under high pressure, it absorbs practically no hydrogen below 40°C. Above 50°C, the absorption of hydrogen becomes remarkable. Hydrogenation of oleic acid in the presence of U–Ni–B gives stearic acid, mainly in the form of its zinc salt. To obtain free stearic acid it is necessary to decompose the salt by boiling with concentrated hydrochloric acid. On the contrary, no salt formation is observed with U–Ni–A, and on distillation of the filtrate of the product, a crude stearic acid is readily obtained as a solid remainder.[23] Hence, U–Ni–A is preferred for this purpose.

Cis isomers are generally more susceptible to hydrogenation than the corresponding *trans* isomers in the presence of Urushibara nickel catalysts. The trend is only observable when the amount of catalyst is small (see Section 6. 6).

Unsaturated ketones can be reduced to saturated alcohols. In neutral solution at room temperature, however, the carbonyl group is reduced only with difficulty. This is utilized in establishing a method for the selective hydrogenation of unsaturated ketones to saturated ketones (see Section 6. 5. 2).

Acetylenic compounds absorb two moles of hydrogen in the presence of Urushibara nickel catalysts and give saturated compounds. In the hydrogenation of propargyl alcohol under ordinary pressure, it is found that the second stage of hydrogen uptake proceeds faster than the first stage, so that the overall hydrogenation rate rapidly increases near the end point of the reaction.[18]

The partial hydrogenation of acetylenic compounds to ethylenic compounds can not be effected by ordinary Urushibara nickel catalysts, because their activities are too high. For instance, 2-butyne-1,4-diol is readily hydrogenated to 1,4-butanediol even in the presence of U–Ni–A(s)(HCl) of comparatively low activity. In contrast, U–Fe catalyst is quite useful for the partial hydrogenation, and easily gives *cis*-

of Ethylenic Compounds

Time (hr)	Flow rate of sample (g/min)	Product	Yield (%)	Reference
3	0.08	ethylbenzene	88	15)
4	0.029	ethylbenzene	91	26)
2	0.073	ethylcyclohexane	94	26)

2-butene-1,4-diol. The U–Co catalyst also serves the same purpose, and effects partial hydrogenation provided the reaction is interrupted at the stage where just one mole of hydrogen is absorbed (see Section 6. 5. 4).

As seen in Table 8–3, styrene gives ethylbenzene in a good yield in vapor-phase hydrogenation, but it can also be hydrogenated to ethylcyclohexane under special reaction conditions.

8. 1. 2. Hydrogenation of Aromatic Rings

Aromatic ring hydrogenation does not proceed under ordinary pressure; it can be effected only at a high temperature and pressure. Under ordinary conditions, U–Ni–A and U–Ni–B can not catalyze the ring hydrogenation of aromatic hydrocarbons, and U–Ni–BA is employed instead.

The inefficiency of U–Ni–A and U–Ni–B does not imply that they are inactive for ring hydrogenation. Rather, it is the consequence of the poisoning action of oxygen-containing solvents, such as water or ethanol. In fact, hydrogenation may proceed in the presence of U–Ni–A with a quantitative absorption of hydrogen provided the catalyst is quite free from water, and that the reaction is carried out in a hydrocarbon solvent such as cyclohexane[33) 40)] (see Section 6. 7). In the case of U–Ni–BA, however, we need not worry about the choice of solvent, and ring hydrogenation can easily be effected even in an ethanol solvent.

Much information about the ring hydrogenation of aromatic compounds is presented in Table 8–4.

Biphenyl absorbs only half the theoretical amount of hydrogen, even in the presence of U–Ni–BA, and the product is cyclohexylbenzene. The hydrogenation of naphthalene proceeds in the presence of U–Ni–B, but tetralin is the only product.

Of all the aromatic compounds, phenols are the only substances

Table 8–4. Hydrogenation of Aromatic

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent	Initial pressure (kg/cm²)
	mole	g				
benzene	0.13	10	U-Ni-BA	2	ethanol	100
„	0.27	21	U-Ni-BA	2	none	80
„		7.8	U-Ni-BA*	2	ethanol	80
„	0.169	13.2	U-Ni-A[b]	1	cyclohexane	40
toluene		9.2	U-Ni-BA*	2	ethanol	80
„	0.141	13.0	U-Ni-A[b]	1	methyl-cyclohexane	40
ethylbenzene	0.09	10	U-Ni-BA	2	ethanol	70
„		10.6	U-Ni-BA*	2	ethanol	75
cumene	0.323	39.0	U-Ni-A[b]	1	none	40
biphenyl		9.3	U-Ni-BA*	2	ethanol	79
naphthalene	0.05	6.4	U-Ni-B	2	ethanol	50
phenol	0.21	20	U-Ni-B	1	ethanol	69
„	0.11	10	U-Ni-BA	2	ethanol	66
„		9.4	U-Ni-BA*	2	ethanol	75
o-cresol	0.51	55	U-Ni-B	2	ethanol	66
„		10.8	U-Ni-BA*	2	ethanol	70
m-cresol		10.8	U-Ni-BA*	2	ethanol	70
anisole		10.8	U-Ni-BA*	2	ethanol	75
resorcinol	0.5	55	U-Ni-B	2	water[c]	69
hydroquinone	0.46	50.5	U-Ni-B	2	ethanol	54
β-naphthol	0.1	14.4	U-Ni-B	2	ethanol	57
bisphenol A		10	U-Ni-BA*	2	ethanol	77
diphenyl ether		11	U-Ni-BA*	2	ethanol	83
methyl benzoate		9	U-Ni-BA*	2	ethanol	61
ethyl benzoate	0.07	10	U-Ni-BA	2	ethanol	54
„	0.07	10	U-Ni-BA*	2	ethanol	55
isopropyl benzoate		11	U-Ni-BA*	2	ethanol	50
phenyl benzoate		9	U-Ni-BA*	2	ethanol	70
diethyl phthalate	0.05	10	U-Ni-BA	2	ethanol	68
„		13.2	U-Ni-BA*	2	ethanol	80
diethyl terephthalate		13.2	U-Ni-BA*	2	ethanol	62

Rings under High Pressure

Temperature (°C)	Time (hr)	Product	Yield (%)	Hydrogen uptake[a] (%)	Reference
100–142	3	cyclohexane	70		31)
90–150	2.5	„	77		31)
100–170	2	„		100	
80–120	2	„		100	
100–170	2	methylcyclohexane		80	
130–140	1.5	„		100	
100–143	4	ethylcyclohexane	63		31)
100–170	2	„		80	
155	2.5	isopropylcyclohexane		100	
100–150	0.8	cyclohexylbenzene		50	
120–150	1.5	tetralin	79		22)
130–150	3.2	cyclohexanol	80		23)
70–110	1	„	79		31)
70–140	0.8	„		100	
180–200	5	2-methylcyclohexanol	46		22)
70–140	1	„		100	
70–140	1	3-methylcyclohexanol		100	
100–160	1	methoxycyclohexane		90	
49–50	17.5	dihydroresorcinol	84		23)
90–150	2	1,4-cyclohexanediol	84		23)
90–110	2.5	*ac*-tetrahydro-β-naphthol	44.2		23)
		ar-tetrahydro-β-naphthol	45.5		
100–165	2	hexahydrobisphenol A		43	
100–150	0.8	cyclohexanol + cyclohexane[d]		100	
100–150	1.5	methyl hexahydrobenzoate		70	
106–150	2.5	ethyl hexahydrobenzoate	82		31)
100–150	1.5	„		70	
100–150	1.5	isopropyl hexahydrobenzoate		70	
130–190	1.5	ethyl hexahydrobenzoate[e] + cyclohexanol		100	
114–154	3	diethyl hexahydrophthalate	91		31)
100–170	1.5	„		100	
100–170	1.5	diethyl hexahydroterephthalate		20	

Continued . . .

Table 8–4.

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent	Initial pressure (kg/cm²)
	mole	g				
salicylic acid		9.2	U–Ni–BA*	2	ethanol	65
methyl salicylate	0.07	10	U–Ni–BA	2	ethanol	65
„	0.07	10	U–Ni–BA*	2	ethanol	58
ethyl salicylate		11.5	U–Ni–BA*	2	ethanol	78
„		10.9	U–Ni–BA*	2	cyclohexane	55
isopropyl salicylate		11.5	U–Ni–BA*	2	ethanol	58
phenyl salicylate		10	U–Ni–BA*	2	ethanol	66
„		7.1	U–Ni–BA*	2	cyclohexane	80
ethyl *o*–ethoxybenzoate		10	U–Ni–BA*	2	ethanol	78
aniline	0.11	10	U–Ni–BA	2	ethanol	96
„	0.11	10	U–Ni–BA	2	ethanol	75
„	0.11	10	U–Ni–BA	2	cyclohexane	70
acetanilide	0.07	10	U–Ni–BA	2	ethanol	75
pyridine	0.1	10	U–Ni–BA	2	cyclohexane	65
furfural	0.33	32	U–Ni–B	2	ethanol	69

* Asterisked catalysts were prepared according to the modified method described in Preparation 17, Chapter 4. Other U–Ni–BA catalysts were prepared by either of Preparations 15 and 16, Chapter 4.

[a] Volume of absorbed hydrogen, relative to the theoretical.

[b] Water was completely excluded by washing the catalyst five times with isopropyl alcohol and then five times with either the solvent for hydrogenation or the material to be hydrogenated.

susceptible to ring hydrogenation, even in the presence of U–Ni–A or U–Ni–B.[23] They can, however, be hydrogenated at lower temperatures and in a shorter time if U–Ni–BA is used.[31]

It is well known that the hydrogenation of phenols is generally favored by the presence of very small amounts of alkali.*[1] U–Ni–B and U–Ni–BA are particularly useful for the hydrogenation of phenols, because their preparation involves alkali treatment as the final operation,

*1) H. E. Ungnade and D. V. Nightingale, *J. Amer. Chem. Soc.*, **66**, 1218 (1944).

Continued.

Temperature (°C)	Time (hr)	Product	Yield (%)	Hydrogen uptake[a] (%)	Reference
100–160	1.5	—		0	
84–115	2	ethyl hexahydrosalicylate[e]	65		31)
100–160	1.5	„		62	
100–170	2	ethyl hexahydrosalicylate		70	
100–160	1.5	„		100	
100–160	1.5	isopropyl hexahydrosalicylate		62	
150–200	2	ethyl hexahydrosalicylate[d] +cyclohexanol		100	
130–170	1.5	—		10	
100–170	2	ethyl 2-ethoxycyclohexane-carboxylate		100	
150–209	3.5	*N*-ethylcyclohexylamine[f] dicyclohexylamine	71		31)
150–208	3	*N*-ethylcyclohexylamine[f] dicyclohexylamine	69		31)
150–215	3	cyclohexylamine dicyclohexylamine	35 38		31)
120–206	5	*N*-acetylcyclohexylamine	77		31)
150–218	3	piperidine	86		31)
70–160	5	tetrahydrofurfuryl alcohol	76		22)

[c] Solution of 24 g of NaOH in 100 ml of water.
[d] Hydrogenolysis took place.
[e] Transesterification was observed during the hydrogenation.
[f] *N*-Ethylation was observed during the hydrogenation.

and hence the catalysts necessarily contain very small amounts of alkali to the extent that, under liquid-phase hydrogenation, the solution becomes weakly alkaline (showing a pink color to phenolphthalein) in the former case, and faintly alkaline (almost insensitive to phenolphthalein) in the latter. There are also cases in which a further appropriate amount of alkali is to be added, according to the type of phenol being treated.

The catalytic hydrogenation of phenols in the presence of U–Ni–B, in general, requires a rather high temperature; however, the efficiency

Table 8–5. Vapor-phase

Compound	Weight of sample (g)	Catalyst	Nickel content (g)	Temperature (°C)
benzene	5	U–Ni–AA	8	176
styrene	5	U–Ni–AA	8	150
phenol	10	U–Ni–BA	4	185
„	5	U–Ni–AA	8	180
acetophenone	5	U–Ni–AA	8	190

of the hydrogenation is satisfactory. Phenol is hydrogenated to cyclohexanol at 130–150°C, and hydroquinone to a mixture of *cis-trans* isomers of 1,4-cyclohexanediol at 90–150°C. The result of the catalytic hydrogenation of hydroquinone is similar to that found in the literature*1) for other nickel catalysts. The catalytic hydrogenation of resorcinol in an alkaline medium in the presence of U–Ni–B gives dihydroresorcinol (1,3-cyclohexanedione), under the same conditions as described in *Organic Syntheses*,*2) which deals with the hydrogenation of the same substance by a Raney nickel catalyst. The yields for both hydrogenations are quite comparable.

It is already known*3) that the catalytic hydrogenation of β-naphthol gives a mixture of *ac*-tetrahydro-β-naphthol and *ar*-tetrahydro-β-naphthol, where the ratio of the products varies according to the alkalinity of the solution. This is also the case with U–Ni–B; thoroughly washed U–Ni–B in neutral ethanol gives a mixed product of almost equal portions.

Ordinary phenols are hydrogenated almost quantitatively in the presence of U–Ni–BA at about 100°C. The hydrogenation of phenol ethers requires a somewhat higher temperature. Diphenyl ether undergoes hydrogenolysis and gives a mixture of cyclohexanol and

*1) L. Palfray, *Bull. Soc. Chim. France*, **7**, 401 (1940); S. Fujita, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **23A**, 399 (1942); *Chem. Abst.*, **44**, 3445 (1950); E. deRuiter and J. C. Jungers, *Bull. Soc. Chim. Berges*, **58**, 210 (1949); *Chem. Abst.*, **45**, 8465 (1951); R. C. Olberg, H. Pines, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **66**, 1097 (1944).

*2) Organic Syntheses, Vol. 27, p. 21 (1947); Coll. Vol. 3, p. 278 (1955).

*3) G. Stork, *J. Amer. Chem. Soc.*, **69**, 576 (1947); H. Adkins and G. Fresek, *ibid.*, **70**, 412 (1948); H. J. Dauben Jr., B. C. McKusick and G. P. Mueller, *ibid.*, **70**, 4179 (1948).

Hydrogenation of Aromatic Rings

Time (hr)	Flow rate of sample (g/min)	Product	Yield (%)	Reference
2 1/3	0.05	cyclohexane	83	26)
2	0.07	ethylcyclohexane	94	26)
6	0.03	cyclohexanol	79	26)
3 1/2	0.111	"	66	26)
1 1/5	0.07	ethylcyclohexane	71	26)

cyclohexane. Bisphenol A absorbs only half the theoretical amount of hydrogen, which corresponds to the hydrogenation of one benzene ring, and the product is indeed a hexahydro compound. Perhaps a steric effect plays a part in the hydrogenation.

Esters of aromatic carboxylic acids can not be hydrogenated in the presence of either U–Ni–B or U–Ni–A; they give the corresponding hexahydro compounds when hydrogenation is carried out in the presence of U–Ni–BA at high temperatures. Hydrogenation tends to be suppressed as the alkyl group of the ester becomes bulky. In particular, the hydrogenation of phenyl benzoate is quite difficult, and the absorption of hydrogen begins only above 170°C if hydrogenated in ethanol. The product is a mixture of ethyl hexahydrobenzoate and cyclohexanol, showing that hydrogenation is accompanied by transesterification. Moreover, phenyl benzoate does not absorb hydrogen even at high temperatures if hydrogenation is carried out in cyclohexane.

In spite of the presence of a phenolic hydroxyl group, salicylic acid, particularly in the form of the free acid, withstands hydrogenation. Its ester may undergo hydrogenation in the presence of U–Ni–BA, but to a lesser extent compared with the benzoate or phthalate. Moreover, the ethyl ether of a salicylic ester is more readily hydrogenated than a salicylic ester with a free OH group. It is suggested that chelation exists between the OH group and the alkoxycarbonyl group, which may affect the susceptibility to ring hydrogenation. Both methyl salicylate and phenyl salicylate, when hydrogenated in ethanol, give the ethyl ester of saturated carboxylic acid, which indicates that transesterification takes place during the course of the hydrogenation. An appreciable amount of the methyl ester also exists in the hydrogenation products of methyl salicylate, but the phenyl ester is completely absent in the hydrogenation products of the phenyl ester.

Table 8–6. Reduction of Carbonyl

Compound	Amount of sample		Catalyst	Nickel content (g)
	mole	g		
acetone	0.02	1.16	U–Ni–B	0.5
cyclohexanone	0.02	1.96	U–Ni–B	0.5
„	0.02	1.96	U–Ni–A	0.4
„	0.02	1.96	U–Ni–A[a]	0.4
benzaldehyde	0.02	2.02	U–Ni–B	0.5
acetophenone	0.02	2.40	U–Ni–B	0.5
benzophenone	0.02	3.64	U–Ni–B	0.5

[a] Obtained by treating the precipitated nickel with propionic acid.
[b] 0.2 millimole (8 mg) of NaOH was added.

Aniline undergoes ring hydrogenation in the presence of U–Ni–BA, but gives a considerable amount of dicyclohexylamine together with the normal product, cyclohexylamine. It has been confirmed that, on hydrogenation in ethanol, it undergoes *N*-ethylation during hydrogenation to give *N*-ethylcyclohexylamine.*1)

At a high temperature, aromatic heterocycles, such as pyridine and furfural, can undergo ring hydrogenation in the presence of U–Ni–BA or U–Ni–B, and give saturated hexahydro or tetrahydro compounds.

The proper choice of an Urushibara nickel catalyst permits the vapor-phase hydrogenation of aromatic rings. Table 8–5 provides some examples. As is shown in the table, styrene and acetophenone are hydrogenated in the vapor phase by U–Ni–A or U–Ni–BA only at the side chain ethylenic bond or carbonyl group, but they are completely hydrogenated to ethylcyclohexane in the presence of U–Ni–AA.[26]

8. 1. 3. Reduction of Carbonyl Compounds

Aldehydes and ketones are easily reduced to the corresponding alcohols in the presence of any Urushibara nickel catalyst. Much information is now available regarding the activities of different Urushibara catalysts, and the optimum reduction conditions in their presence under ordinary or high pressures, particularly for the reduction of ketones, such as cyclohexanone or benzophenone. Ketones have the marked advantage that they are quite free from any complications in the reduction (see Sections 6. 1, 6. 2 and 6. 4).

*1) H. I. Cramer and H. Adkins, *J. Amer. Chem. Soc.*, **52**, 4354 (1930).

Compounds under Atmospheric Pressure

Solvent (ethanol) (ml)	Temperature (°C)	Time (hr)	Product	Reference
20	25	105	isopropyl alcohol	18)
20	25	44	cyclohexanol	18)
20[b]	25	40	"	
20[b]	25	20	"	
20	25	38	benzyl alcohol	22)
20	25	85	1-phenylethanol	18)
20	25	95	benzhydrol	18)

Delépine and Horeau have shown that the presence of a trace amount of alkali greatly enhances the reduction of carbonyl compounds by Raney nickel.*1) This is also the case with Urushibara nickel.

In the case of U–Ni–B, the best result is secured when the catalyst is washed with water and ethanol to such an extent that the solution of the reaction mixture is faintly alkaline to phenolphthalein. U–Ni–B, prepared according to Preparation 3, Chapter 4, contains just that amount of alkali which is appropriate for the reduction of carbonyl compounds. In the case of U–Ni–A, a very small amount of alkali must be added for the same purpose.

A great deal of information is available with regard to the amount of alkali to be added[19] (see Section 6. 1 (*c*)), which indicates that the reduction rate is maximum when 0.004 g of sodium hydroxide is added for every 0.2 g of nickel in the catalyst. It was found that a greater amount of alkali tends to retard the reaction, and an excess amount may often suppress it.

The liquid-phase reduction of carbonyl compounds may take place at room temperature, but a high temperature is preferred because the reduction rate is greatly enhanced. Under high pressure, reduction is best conducted at 60–70°C, where a steep rise in the reduction rate is observed.[14) 34)] The initial pressure of hydrogen has little effect on the reaction rate within the range 30 to 120 kg/cm^2.

U–Co–A and U–Co–B are also useful in the reduction of ketones, but the rate of reduction is considerably lower than with Urushibara

*1) M. Delépine and A. Horeau, *Bull. Soc. Chim. France*, [5] **4**, 31 (1937).

Table 8–7. Reduction of Carbonyl

Compound	Amount of sample		Catalyst	Weight of catalyst metal (g)	Solvent (ethanol) (ml)	pH
	mole	g				
acetone	0.2	11.9	U-Ni-B	2		9–10
„	2.0	116	U-Ni-B	2	none	9–10
cyclohexanone	0.2	19.6	U-Ni-B	2		9–10
„	0.4	39.2	U-Ni-B	2		9–10
benzaldehyde	0.14	15	U-Ni-B	3.5		—
acetophenone	0.2	24	U-Ni-B	2		9–10
„	0.25	30	U-Ni-B	1	60	9–10
„	„	„	U-Ni-A	1	„	9.2–10[a]
„	„	„	U-Ni-BA	1	„	9.4–10.4
„	„	„	U-Ni-CB	1	„	9.7–10.7
„	„	„	U-Ni-CA	1	„	9.4–9.6[a]
propiophenone	0.65	86.5	U-Ni-B	2		9–10
benzophenone	0.1	18.2	U-Ni-B	2		9–10
„	0.1	18.2	U-Ni-B	2		9–10
„	0.07	12.74	U-Ni-B	1	110	9.3–9.7
„	„	„	U-Ni-A	1	„	10–10.5[b]
„	„	„	U-Ni-BA	1	„	10.5–10.6
„	„	„	U-Ni-CB	1	„	10–10.7
„	„	„	U-Ni-CA	1	„	9.8–10.5[b]
„	„	„	U-Co-B	1	„	9–10.4
„	„	„	U-Co-A	1	„	10.1–10.4[b]
„	„	„	U-Cu	1	55	9.5–10[b]
deoxybenzoin	0.05	9.8	U-Ni-B	0.5	50	9–11
„	„	„	U-Ni-A	0.5	„	„ [c]
„	„	„	U-Ni-CB	0.5	„	„
„	„	„	U-Ni-CA	0.5	„	„ [c]
benzoin	0.05	10.6	U-Ni-B	0.5	50	9–11
„	„	„	U-Ni-A	0.5	„	„ [c]
„	„	„	U-Ni-CB	0.5	„	„
„	„	„	U-Ni-A(s)	0.5	„	„ [c]
„	„	„	U-Cu-C	1	„	„ [c]
benzil	0.05	10.5	U-Ni-B	0.5	50	9–11
„	„	„	U-Ni-A	0.5	„	„ [c]
„	„	„	U-Ni-CB	0.5	„	„
„	„	„	U-Cu-C	1	„	„ [c]
„	„	„	U-Ni-A	0.5	„	„ [c]
„	„	„	U-Ni-A(s)	0.5	„	„ [c]
furil	0.05	9.5	U-Ni-A	0.5	50	9–11[c]
„	„	„	U-Ni-A(s)	0.5	„	„ [c]

[a] 1 ml of 10% NaOH was added.
[b] 0.5 ml of 10% NaOH was added.
[c] 0.5 ml of 5% NaOH was added.

Compounds under High Pressure

Initial pressure (kg/cm²)	Temperature (°C)	Time (min)	Product	Yield (%)	Reference
50	16	120	isopropyl alcohol		14)
100	64–78	90	„	90	„
100	15–70	120	cyclohexanol	87	„
50	60–90	120	„	82	„
50	30–50	90	benzyl alcohol	48	„
50	60–114	120	1-phenylethanol	86	„
45–50	60–70	70–125	„	91–95	36)
45–49	60–70	25–40	„	„	„
40–45	60–70	95–120	„	„	„
49–50	61–69	50–65	„	„	„
42–49	61–70	40–50	„	„	„
52	60–90	120	1-phenyl-1-propanol	85	14)
50	60–70	60	benzhydrol	82	„
50	25–175	90	diphenylmethane	85	„
30–50	58–68	25–75	benzhydrol	90–95	34)
46–52	59–63	6–12	„	„	„
45–50	60–66	35–45	„	„	„
50–60	60–70	10–35	„	„	„
40–60	60–70	10–20	„	„	„
50–56	60–69	65–70	„	90	„
45–50	59–66	45–50	„	90	„
40–53	100–120	40–65	„	96	„
56	60–62	30	1,2-diphenylethanol	91–94	37)
56	60–61	17	„	„	„
58	62–65	18	„	„	„
60	60–63	22	„	„	„
55	60–65	50	hydrobenzoin	90–93	„
55	65–67	10	„	„	„
60	60–61	50	„	„	„
57	61–64	25	„	„	„
38	130–132	30	„	„	„
93	60–64	120	hydrobenzoin	90	37)
95	60–66	25	„	„	„
101	59–66	95	„	„	„
80	128–138	55	„	„	„
80	20	100	benzoin	76	„
85	22	115	„	80	„
56	60–63	90	furoin	81	„
60	60–62	100	„	79	„

Table 8–8. Vapor-phase Reduction

Compound	Weight of sample (g)	Catalyst	Nickel content (g)	Temperature (°C)
acetophenone	9.9	U–Ni–A	4	200
„	5	U–Ni–BA[a]	3	200
„	5	U–Ni–AA	8	190

[a] "Hyflosupercel" was used as a carrier.

nickel catalysts. The Urushibara copper catalysts allows complete reduction only at a temperature as high as 120°C.

Typical examples are shown in Table 8–6 and 8–7.

Carbonyl compounds are easily reduced to the corresponding alcohols under ordinary conditions. Benzophenone is reduced to diphenylmethane at a higher temperature[14] (see Section 6. 2). α-Diketones, such as benzil or furil, give diols on complete reduction, but they may undergo partial reduction giving the α-hydroxy ketones, benzoin and furoin, if the reaction is interrupted after just one mole of hydrogen has been absorbed, when a sudden fall in the absorption rate is observed[37] (see Section 6. 5. 5). Urushibara nickel catalysts can also be applied to the reduction of steroid ketones with good results, of which a survey is given in a later section (Section 8. 1. 10).

Ketones are also reduced in the vapor phase. Table 8–8 shows the vapor-phase reduction of acetophenone, where the carbonyl group is converted to a methylene group; even ring hydrogenation may take place, depending on the conditions employed.[26]

8. 1. 4. Reduction of Aromatic Nitro Compounds

Subject to proper conditions, aromatic nitro compounds are easily reduced to amino compounds in the presence of Urushibara catalysts. The presence of alkali interferes with the reduction of a nitro group to an amino group, thereby resulting in diverse products depending on the type of Urushibara nickel catalyst or reaction conditions employed. For example, nitrobenzene absorbs an indefinite amount of hydrogen either under ordinary pressure or under high pressure, giving azobenzene and azoxybenzene (to some extent at the expense of aniline) if it is reduced in the presence of U–Ni–B prepared by the standard process, so that it contains a small amount of alkali. On the other hand, it gives aniline in good yield in the presence of U–Ni–B which has been washed free

of a Carbonyl Compound

Time (hr)	Flow rate of sample (g/min)	Product	Yield (%)	Reference
3 ½	0.06	ethylbenzene	90	15)
1 ¾	0.114	„	52	26)
2	0.069	ethylcyclohexane	71	26)

from alkali so that the pH of the reactant solution is below 8, or in the presence of U–Ni–A, which always causes the pH of the solution to be 6–7. In order that the reduction of nitro compounds may proceed effectively with U–Ni–B prepared according to Preparation 3, Chapter 4, it is necessary to wash the catalyst more than ten times with 40 ml portions of distilled water at 50–60°C (the distilled water should be boiled before use). Washing should be by decantation, as this allows a rapid operation so that the lowering of activity can be maximally avoided. The number of times the catalyst is washed with water may be reduced to four or five if the catalyst is treated at 50–60°C with saturated sodium chloride solution before washing with water.

The effect of pH on the efficiency of the high pressure reduction of nitrobenzene is given in Table 8–10. In the presence of U–Ni–A, the addition of sodium hydroxide to give a pH above 10 greatly reduces the yield of aniline, with additional production of undesirable products such as azobenzene, azoxybenzene, and an unidentified resin. At pH 6–7, the yield of aniline is satisfactory. The addition of acetic acid to give a pH below 3, on the other hand, paralyzes the catalytic activity, and the reduction is quite incomplete.

Tables 8–9 through 8–11 show the results of the reduction of a number of nitro compounds under either ordinary or high pressures. Table 8–9 includes *p*-nitrosophenol to illustrate the reduction of nitroso compounds, which, as we see, also proceeds in a similar manner in the presence of Urushibara nickel catalysts.

The large scale reduction of nitro compounds under ordinary pressure requires a somewhat complicated treatment. It is necessary to make a provision for sufficient cooling of the reactor to prevent an undesirable rise in temperature, or to begin with a small amount of catalyst, with supplemental addition at every fall in catalytic activity, since the presence from the beginning of a large amount of catalyst tends to cause a strong

Table 8–9. Reduction of Aromatic Nitro and

Compound	Amount of sample		Catalyst	Nickel content (g)
	mole	g		
nitrobenzene	0.0066	0.821	U-Ni-B	0.5
„	„	„	U-Ni-A	0.4
„	„	„	U-Ni-A[b]	0.4
„	20[a]	2500	U-Ni-A	450
o-nitrotoluene	0.0066	0.914	U-Ni-B	0.5
„	0.5	67.1	U-Ni-A	2+1.5[c]
p-nitrotoluene	0.0066	0.914	U-Ni-B	0.5
„	10[a]	1400	U-Ni-A	250
p-nitroaniline	10[a]	1400	U-Ni-A	300
ethyl *m*-nitrobenzoate	0.0066	1.30	U-Ni-B	0.5
m-nitroacetophenone	0.0066	1.10	U-Ni-B	0.5
2-nitro-*p*-cymene	0.5	84.6	U-Ni-A	3+2[c]
4-nitroresorcinol	0.015	2.4	U-Ni-A	0.5
p-nitrosophenol	10[a]	1000	U-Ni-A	250

[a] Test experiment for the industrial application of Urushibara catalysts. Special devices were employed in the preparation of the catalyst and in conducting the reduction.

[b] Prepared by treating the precipitated nickel with propionic acid.

Table 8–10. Reduction of Nitroben-

Amount of sample		Catalyst	Nickel content (g)	Solvent (ethanol) (ml)	pH[b]	Initial pressure (kg/cm²)
mole	g					
0.3	37.5	U-Ni-B[a]	2	100	8.2	50
0.3	37.5	U-Ni-B[a]	2	100	7.4	49
0.2	25	U-Ni-A	0.5	30	>10	80
0.2	25	U-Ni-A	1	30	>10	60
0.2	25	U-Ni-A	0.5	30	ca. 7	100
0.2	26	U-Ni-A	1	50	6–7	130
0.2	26	U-Ni-A	2	50	6–7	122
0.2	25	U-Ni-A	4	50	6–7	100
0.2	25	U-Ni-A	0.5	40	3	99

[a] Alkali was removed as completely as possible by warming with NaCl solution at 60°C, followed by thorough washing.

[b] pH was adjusted by adding either NaOH or acetic acid.

[c] Heat was not applied. The temperature rose spontaneously owing to the heat of reaction.

Nitroso Compounds under Atmospheric Pressure

Solvent (ml)		Temperature (°C)	Time (min)	Product	Yield (%)	Reference
ethanol	20	25	20	aniline		18)
ethanol	20	25	25	„		22)
ethanol	20	25	19	„		22)
none		80–90	600	„	97.1	
ethanol	20	25	22	*o*–toluidine		18)
ethanol	100	25–30	320	„	84	22)
ethanol	20	25	24	*p*–toluidine		18)
methanol	2000	64	250	„	90.5	
methanol	2000	64	270	*p*–phenylenediamine	86.5	
ethanol	20	25	32	ethyl *m*–aminobenzoate		18)
ethanol	20	25	37	*m*–aminoacetophenone		18)
ethanol	100	25–30	480	carvacrylamine	72	22)
ethanol	30	room temp.	—	4–aminoresorcinol[d]		11)
methanol	2000	25–30	300	*p*–aminophenol	82.5	

[c] A supplemental amount of catalyst was added in the course of reduction.

[d] Very unstable material. It was subjected to the succeeding reaction without being isolated.

zene under High Pressure

Maximum temperature (°C)	Time (min)	Product (%)		
		aniline	azobenzene	remarks
80	85	71	?	
117	60	90	—	
172	80	19	17	resinous matter
152	180	32	64	resinous matter
94	80	76	22[d]	
80	45	92	—	
72	45	91	—	
38[e]	90	93	—	
180	180	12	2	nitrobenzene recovered[e] (74%)

[d] Containing a considerable amount of azoxybenzene.

[e] Catalytic activity was lost owing to the formation of $Ni(CH_3CO_2)_2$ from nickel and acetic acid, which was added in large amount. A part of the solvent was converted to ethyl acetate and gave off an ester odor.

Table 8–11. Reduction of Aromatic Nitro

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent (ethanol) (ml)
	mole	g			
o–nitrotoluene	0.1	13.7	U–Ni–A	1	50
p–nitrotoluene	0.1	13.7	U–Ni–A	1	50
m–dinitrobenzene	0.05	8.4	U–Ni–A	1	50
2,4–dinitrotoluene	0.03	5.5	U–Ni–A	0.5	130
1,5–dinitronaphthalene	0.05	10.9	U–Ni–A	1	60
m–nitrobenzaldehyde	0.1	15.1	U–Ni–A	1	50[a]
p–nitrobenzaldehyde	0.04	6.6	U–Ni–A	1	45[a]
m–nitroacetophenone	0.1	16.5	U–Ni–A	1	40
"	"	"	U–Ni–A	0.5	40
"	"	"	U–Ni–A	0.5	40
"	"	"	U–Ni–A	1	45
p–nitroacetophenone	0.03	4.5	U–Ni–A	0.5	65
3–nitro–4–methylacetophenone	0.1	18	U–Ni–A	1	50
ethyl *p*–nitrobenzoate	0.05	9	U–Ni–A	1	50

[a] Dimethylaniline was used as the solvent instead of ethanol.

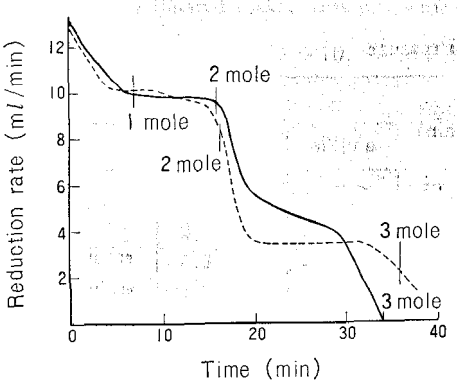


Fig. 8–1. Reduction of Ethyl *m*–Nitrobenzoate and *m*–Nitroacetophenone under Atmospheric Pressure in the Presence of U–Ni–B

——— Ethyl *m*-nitrobenzoate; ..... *m*-Nitroacetophenone
Sample: $1/3 \times 10^{-2}$ mole
Catalyst: U–Ni–B, containing 0.25 g of Ni
Solvent: ethanol, 20 ml
Conditions: atmospheric pressure, 25°C

Compounds under High Pressure

pH	Initial pressure (kg/cm²)	Temperature (°C)	Time (min)	Product	Yield (%)	Reference
6–7	78	85	120	*o*-toluidine	88	22)
6–7	79	76	120	*p*-toluidine	97	22)
6–7	80	45–72	100	*m*-phenylenediamine	82	
6–7	80	45–72	160	2,4-toluenediamine	92	
6–7	75	110	100	1,5-naphthalenediamine		
6–7	78	52–82	120	*m*-aminobenzyl alcohol	32	
6–7	48	55–67	30	*p*-aminobenzyl alcohol	50	
6–7	70	128	120	*m*-aminoacetophenone	92	22)
6	60	80	140	„	86	
6.2	70	105	120	„	89	
6–7	63	48–142	200	1-(*m*-aminophenyl)ethanol	80	
6–7	55	40–112	150	*p*-ethylaniline	16	
6–7	80	102	60	3-amino-4-methylacetophenone	93	22)
6–7	100	98	80	ethyl *p*-aminobenzoate	96	22)

reaction, making the temperature go above 40°C, which in turn often causes the rapid destruction of catalytic activity.

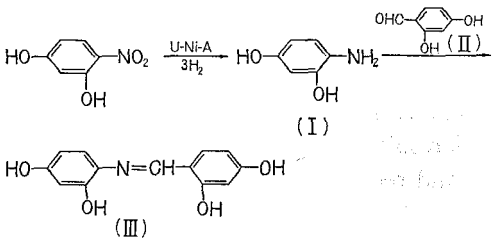
Free carboxylic acid paralyzes the activity of a nickel catalyst, so that *m*-nitrobenzoic acid in an ethanol solution, or even its sodium salt in an aqueous solution, for instance, is reduced only with great difficulty. Good results are secured only when the acid is converted to its ethyl ester and reduced in an ethanol solution.

Figure 8-1 shows the rate of reduction of ethyl *m*-nitrobenzoate and *m*-nitroacetophenone under ordinary pressure in the presence of U-Ni-B which has been treated with sodium chloride solution. The rate of absorption of the first two moles of hydrogen is comparatively high, but a prompt fall comes at the end of this stage when the uptake of another mole of hydrogen begins to take place.[18] In the case of *m*-nitroacetophenone an additional step follows, in which the carbonyl group is reduced with the further uptake of one mole of hydrogen. In this case the rate of the uptake of the last mole of hydrogen is very slow; so that one can easily interrupt the reduction at the stage when just three moles of hydrogen have been absorbed, to obtain *m*-aminoacetophenone in a good yield.

Contrary to the case of nitro groups, the reduction of carbonyl

groups is accelerated by the presence of alkali. This enables us to realize the selective reduction of nitro groups in nitro ketones by employing U–Ni–A or alkali-free U–Ni–B. High temperatures are to be avoided in the selective reduction, as we see for nitroacetophenones in Table 8–11; these, at low temperatures, give aminoacetophenones in a good yield, but are reduced to alcohols, or even to ethylbenzene derivatives, at high temperatures.

An interesting application of catalytic reduction is found in a synthetic investigation involving the reaction of an unstable amino compound. 4-Aminoresorcinol (I) is a substance, which, on exposure to air, is rapidly oxidized and darkens, and hence can not be isolated in the pure form; so that no description of its melting point or other physical properties can be found in the literature. To obtain an azomethine compound (III) by condensation of 2,4-dihydroxybenzaldehyde (II) and (I), the latter material should be fresh, and the reaction should be carried out as soon as it is prepared. It is reported that (III) can be obtained in a yield as high as 91% when 4-nitroresorcinol is reduced in absolute ethanol under ordinary pressure in the presence of U–Ni–A and the catalyst is separated from the filtrate at the stage where three moles of hydrogen are absorbed; the calculated amount of (II) is then added immediately.[11]



Reduction of nitrobenzene to aniline can be carried out equally well in the vapor phase in the presence of any of U–Ni–AA, U–Ni–BA, or U–Ni–A. It is reported that, in this case, small amounts of various high-molecular amines are formed as by-products[15) 26)] (see Table 7–1, 7–2, and 7–3, Chapter 7).

8. 1. 5. Reduction of Nitriles

Nitriles are reduced to amines in the presence of either an Urushibara nickel catalyst or an Urushibara cobalt catalyst. As is always the case with an ordinary nickel catalyst, the main products are primary amines, but are always accompanied by greater or lesser amounts of

Table 8–12. Reduction of Nitriles and an Oxime under Atmospheric Pressure

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent (ethanol) (ml)	Temperature (°C)	Time (min)	Product	Yield (%)	Reference
	mole	g								
benzonitrile	0.01	1.03	U-Ni-B	0.5	20	25	155	benzylamine dibenzylamine	40–50 20	18)
„	0.1	10.3	U-Ni-A[a]	2.4	20	35–38	330	benzylamine dibenzylamine	78 2.5	
„	0.1	10.3	U-Ni-A	3.2	20	35–38	360	benzylamine dibenzylamine	72.4 4.5	
benzyl cyanide	0.01	1.17	U-Ni-B	0.5	20	25	175	phenethylamine diphenethylamine	— —	18)
„	0.05	5.86	U-Ni-A[b]	1.6	20	35–38	270	phenethylamine	86	
adiponitrile	0.001	0.108	U-Ni-B	0.5	20	25	150	hexamethylenediamine	—	18)
„	0.1	10.8	U-Ni-A[c]	3.2	20	35–38	270	„	81	
cyclohexanone oxime	0.01	1.13	U-Ni-B	0.5	20	25	210	cyclohexylamine	—	18)

[a] 0.15 g of NaOH was added.
[b] 0.10 g of NaOH was added.
[c] 0.20 g of NaOH was added.

Table 8–13. Reduction of Nitriles

Compound	Amount of sample		Catalyst	Nickel or cobalt content (g)	Solvent (ml)	
	mole	g				
benzonitrile	0.145	15	U–Ni–B	3.5	ethanol	85
„	0.145	15	U–Ni–B	3.5	ethanol	85
„	0.1	10.3	U–Ni–B	1	methanol	40
„	0.1	10.3	U–Ni–NH_3	1	methanol	40
„	0.1	10	U–Co–B	0.5	methanol	
benzyl cyanide	0.1	11.7	U–Ni–B	1	methanol	40
„	0.1	11.7	U–Ni–NH_3	1	methanol	40
„	0.05	5.86	U–Ni–A[a]	2	ethanol	20
„	0.085	10	U–Co–B	0.5	methanol	
adiponitrile	0.1	10.8	U–Ni–B	1	methanol	40
„	0.1	10.8	U–Ni–NH_3	1	methanol	40
„	0.1	10.8	U–Ni–NH_3	1	methanol	40
„	0.1	10.8	U–Co–B	1	methanol	40
„	0.09	10	U–Co–B	0.5	methanol	
3,4–dimethoxy-benzyl cyanide	0.06	10	U–Co–B	0.5	ethanol	
„	0.06	10	U–Co–B	0.5	dioxane	
1–cyclohexenylacetonitrile	0.08	10	U–Co–B	0.5	methanol	20
1–cyclopentenylacetonitrile	0.09	10	U–Co–B	0.5	methanol	20
1–cycloheptenylacetonitrile	0.074	10	U–Co–B	0.5	methanol	20

[a] 0.1 g of NaOH was added.

secondary amines. In some cases, aldehydes are also formed under special reduction conditions.

Tables 8–12 and 8–13 show the catalytic reduction of a number of nitriles. Reduction may proceed either under ordinary or high pressure; high pressure is preferred, as the reduction will then proceed more

under High Pressure

Initial pressure (kg/cm²)	Temperature (°C)	Time (min)	Product	Yield (%)	Reference
50	135–150	47	benzylamine dibenzylamine benzaldehyde	57 8.4 7.1	12)
50	40–60	35	benzylamine dibenzylamine benzaldehyde	43 5.6 24.4	12)
100	86	26	benzylamine dibenzylamine	72 20	30)
100	88	27	benzylamine dibenzylamine	68 21	30)
90–100	85–90	—	benzylamine	85	8)
100	92	20	phenethylamine diphenethylamine	79 12	30)
100	82	23	phenethylamine diphenethylamine	84 3	30)
50	35–38	270	phenethylamine	86	
90–100	85–90	—	phenethylamine	83	8)
100	92	80	hexamethylenediamine	59	30)
100	96	40	„	74	„
100	124	30	„	73	„
100	96	50	„	80	„
90–100	85–90		„	85	8)
90–100	85–90		β-(3,4-dimethoxyphenyl)ethylamine	68	„
90–100	85–90		„	86	„
90–100	85–90		β-(1-cyclohexenyl)ethylamine	80	8)
90–100	85–90		β-(1-cyclopentenyl)ethylamine β-cyclopentylethylamine	65	„
90–100	85–90		β-(1-cycloheptenyl)ethylamine β-cycloheptylethylamine	80	„

rapidly. Moreover, the rate of absorption of hydrogen rises steeply at high temperatures, as can be seen in the reduction of benzonitrile[12] (Fig. 6–10), which shows a steep rise in the rate above 40°C. Thus high temperature and pressure are advisable in order to secure effective reductions. Practically, a temperature between 80°C and 100°C

Table 8–14. Vapor-phase

Weight of sample (g)	Catalyst	Nickel content (g)	Carrier	Temperature (°C)
8.0	U-Ni-A	4	pumice stone	250
5.0	U-Ni-AA	8	aluminum	250
8.0	reduced nickel (+copper)	7	kieselguhr	250

[a] M. Tanaka, K. Watanabe, and K. Hata, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **76**, 1392 (1955).

is best employed to allow for experimental convenience.

It is well known that, in the reduction of nitriles by Raney nickel, a proper choice of solvent or the addition of a proper amount of alkali favors the formation of primary amines.*[1] In the case of Urushibara catalysts, U–Ni–B, which always contains a small amount of alkali, is effective, and U–Ni–A with a limited amount of sodium hydroxide added also gives good results (Table 8–12).

The addition of ammonia to Raney nickel has a favorable effect on the formation of primary amines*.[2] This is also the case with the Urushibara nickel catalyst, and U–Ni–NH_3 (Preparation 12, Chapter 4) greatly increases the yields of primary amines.[30] Moreover, it has been shown that, in its presence, the time required to complete the reduction of adiponitrile is greatly shortened.

There is evidence that Raney cobalt is more effective than Raney nickel in producing primary amines.*[3] It has been shown that U–Co–B is more effective yet and has an activity comparable to, or even superior to, that of Raney cobalt.[8,30] The reduction of 3,4-dimethoxybenzyl cyanide (see Table 8–13) has revealed the fact that the efficiency of reduction in the presence of U–Co–B is greatly influenced by the kind of solvent used; for instance, ethanol saturated with ammonia completely destroys the catalytic activity of the Urushibara cobalt catalyst, in contrast to the case of Raney cobalt, where the presence of ammonia does not affect its activity.*[3] We note at this stage, therefore, that U–Co–B catalyst cannot be used when ammonia is present.

*1) M. Fluchaire and F. Chambret, *Bull. Soc. Chim. France*, [5] **11**, 22 (1944).
*2) E. D. Schwoegler and H. Adkins, *J. Amer. Chem. Soc.*, **61**, 3499 (1939).
*3) W. Reeve and W. M. Eareckson, *ibid.*, **72**, 3299 (1950).

Reduction of Benzonitrile

Time (hr)	Flow rate of sample (g/min)	Product	Yield (%)	Reference
3	0.07	toluene benzylamine dibenzylamine	14 29 41	15)
2	0.075	toluene	76	26)
1 2/3	0.079	toluene benzene	87.5 0.8	*a*

It is emphasized that cobalt catalysts are particularly active in the reduction of nitriles, suppressing at the same time the undesirable formation of secondary amines, but are less active than nickel catalysts for hydrogenating ethylenic linkages. Schnider and Hellerbach*1) observed that, in the presence of Raney cobalt, β-(1-cyclohexenyl)-ethylamine was formed in a good yield from 1-cyclohexenylacetonitrile, which, in the presence of Raney nickel, gave only a saturated amine. Saito[8] has shown that U–Co–B also had a like activity in the same reduction, and gave the unsaturated amine in a good yield (see Table 8–13). A somewhat different result is obtained when 1-cyclopentenylacetonitrile or 1-cycloheptenylacetonitrile is reduced under the same conditions, in the presence of U–Co–B or Raney cobalt. In this case considerable amounts of saturated amines are formed as by-products.

It sometimes happens that benzaldehyde is isolated, together with benzylamine and dibenzylamine, in the catalytic reduction of benzonitrile.[12] The mechanism of the reduction of nitriles has been dealt with in many publications.*2) According to these, the first stage involves the formation of aldimines, which are then hydrogenated to primary amines. When a catalyst of low activity is used, or when the activity of the catalyst is diminished as the reaction proceeds, the hydrogenation of aldimines to primary amines is inhibited and a secondary

*1) O. Schnider and J. Hellerbach, *Helv. Chim. Acta*, **33**, 1437 (1950).

*2) G. Mignonac, *Compt. Rend.*, **171**, 114 (1920); H. Rupe and K. Glenz, *Helv. Chim. Acta*, **5**, 937 (1922); J. v. Braun, G. Blessing, and F. Zobel, *Ber.*, **56**, 1988 (1923); R. Juday and H. Adkins, *J. Amer. Chem. Soc.*, **77**, 4559 (1955); M. Obata, K. Watanabe, and K. Hata, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **78**, 116 (1957).

Table 8–15. Reduction of α-Benzaldoxime under High

Amount of sample		Nickel content (g)	Alkaline additive	Amount of additive	
mole	g			mole	g
0.2	24.2	2	none	—	—
0.1	12.1	1	none	—	—
0.1	12.1	1	KOH	1/100	0.6
0.1	12.1	1	KOH	1/50	1.1
0.1	12.1	1	KOH	1/40	1.4
0.1	12.1	1	KOH	1/30	1.9
0.1	12.1	1	KOH	1/20	2.8
0.1	12.1	1	KOH	1/10	5.6
0.1	12.1	1	NH_3	1/30	0.6

[a] Benzaldehyde or benzamide (determined as benzoic acid, after oxidation with alkaline hydrogen peroxide).

reaction, which leads to secondary amines through the formation of Schiff bases, is apt to take place. When water is present, it will react with aldimines and produce aldehydes. The fact that the formation of aldehyde in the reduction of benzonitrile by U–Co–B is limited to experiments which are carried out in an inefficient horizontally shaking autoclave, and also that its formation is particularly remarkable when the reaction temperature is kept as low as 40–60°C, seem to support the above mechanism of reduction.

With regard to vapor-phase reduction, it has been established that aromatic nitriles undergo hydrogenolysis at their cyano groups in the presence of Sabatier's reduced nickel. For instance, benzonitrile gives toluene and ammonia.*1) As for the Urushibara nickel catalysts, U–Ni–AA gives almost the same result,[26] but the result with U–Ni–A is somewhat different.[15] In this case, the formation of toluene is largely suppressed and the main products are benzylamine and dibenzylamine, as in the case of liquid-phase reduction, the formation of the latter being especially increased.

Various aspects of the vapor-phase reduction of benzonitrile will be found in Table 8–14.

8. 1. 6. Reduction of Oximes

The catalytic reduction of oximes has many points in common with

*1) P. Sabatier and J. B. Senderens, *Compt. Rend.*, **140**, 482 (1905); K. Hata and K. Watanabe, *Bull. Chem. Soc. Japan*, **32**, 86 (1959).

Pressure in the Presence of U–Ni–B (Solvent: ethanol, 50–70 ml)

Initial pressure (kg/cm²)	Maximum temperature (°C)	Time (min)	Product and yield (%)		
			benzylamine	dibenzylamine	neutral substance[a]
52	79	70	18	60	—
102	105	30	36	47	3
78	93	25	47	27	3
70	99	25	55	20	—
71	93	30	59	21	—
75	99	30	75	—	3
75	97	20	75	—	3
75	93	20	74	—	7
68	89	30	44	42	—

the reduction of nitriles, giving primary and secondary amines. In the reduction of aldoximes, the formation of the latter is particularly remarkable.*1)

In the high-pressure reduction of α-benzaldoxime in the presence of U–Ni–B, a prompt rise in the reaction rate comes at about 60°C, and the material is easily reduced with the uptake of two moles of hydrogen, giving a mixture of benzylamine and dibenzylamine, the latter being predominant.

Caustic alkali or ammonia favor the formation of primary amines in the catalytic reduction of nitriles or oximes. For example, Fluchaire and Chambret*2) succeeded in effecting the quantitative reduction of nitriles to primary amines by adding a definite amount of sodium hydroxide.

The effect of alkali on the reduction of α-benzaldoxime in the presence of U–Ni–B has been examined in detail.[24] Table 8–15 shows data on this reduction with respect to changes in the amount of alkali added. The table clearly indicates that the addition of potassium hydroxide tends to inhibit the formation of secondary amine, and increases the yield of primary amine. The presence of a 1/30 molar amount of potassium hydroxide completely inhibits the formation of secondary amine and gives primary amine in the highest yield. A trace amount of benzamide is also found in the product, but it pro-

*1) L. Beregi, *Magyar Kém. Folyóirat*, **56**, 257 (1950); *Chem. Abst.*, **46**, 8000 (1952); C. F. Winans and H. Adkins, *J. Amer. Chem. Soc.*, **55**, 2051 (1933).

*2) M. Fluchaire and F. Chambret, *Bull. Soc. Chim. France*, [5] **11**, 22 (1944).

Table 8–16. Reduction of Oximes

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent (ml)	Initial pressure (kg/cm^2)
	mole	g				
α-benzaldoxime	0.1	12.1	U-Ni-B	1	ethanol	102
„	0.1	12.1	U-Ni-B	1	methanol 40	100
„	0.1	12.1	U-Ni-B	1	ethanol[b]	75
„	0.1	12.1	U-Ni-NH_3	1	methanol 40	100
cyclohexanone oxime	0.14	16.0	U-Ni-A	2.5	ethanol	90
acetophenone oxime	0.15	20.3	U-Ni-A	2.5	„	92
benzophenone oxime	0.15	29.6	U-Ni-A	2.5	„	57
„	0.12	23.6	U-Ni-A	2	„	80
„	0.1	19.7	U-Ni-B	1	„	54
„	0.1	19.7	U-Ni-A[a]	1	„	53

[a] Treated with 10% NaOH for 5 minutes, and then washed twice with distilled water at 50–60°C.

bably is formed by the isomerization of aldoxime in the presence of nickel catalyst.*1) The presence of alkali has little effect on the rate of reduction.

The presence of ammonia, instead of potassium hydroxide, also increases the yield of primary amine, but can not prevent the formation of secondary amine. U–Ni–NH_3 has similar properties and can not eliminate the formation of a considerable amount of secondary amine.[30] (Table 8–16).

The catalytic reduction of ketoximes with Urushibara nickel catalysts is best accomplished at high temperature and pressure. Several examples are illustrated in Table 8–16. We see that ketoximes give mainly primary amines in good yields and that the formation of secondary amines is negligible.

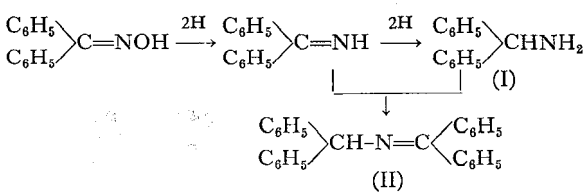
In the reduction of benzophenone oxime, U–Ni–A gives a limited amount of *N*-benzhydrylidene-benzhydrylamine (II), together with the main product, benzhydrylamine (I).

*1) R. Paul, *Compt. Rend.*, **204**, 363 (1937).

under High Pressure

Maximum temperature (°C)	Time (min)	Product	Yield (%)	Reference
105	30	benzylamine dibenzylamine	36 47	24)
90	22	benzylamine dibenzylamine	35 57	30)
99	30	benzylamine	75	24)
90	22	benzylamine dibenzylamine	50 40	30)
80	65	cyclohexylamine	94	24)
101	40	α-phenylethylamine	81	„
84	65	benzhydrylamine *N*-benzhydrylidenebenzhydrylamine	75 17	„
79	70	benzhydrylamine *N*-benzhydrylidenebenzhydrylamine	77 12	„
76	105	benzhydrylamine	93	„
76	110	benzhydrylamine	98	„

[b] 1.9 g (1/30 mole) of KOH was added.



Compound II probably corresponds to a Schiff base, an intermediate in the formation of secondary amines, which is believed to exist in the catalytic reduction of nitriles or aldoximes; hence, it should be formed from benzophenone by a similar mechanism. Such a by-product can not be isolated when U–Ni–B or U–Ni–A treated with sodium hydroxide is used instead, and the yield of benzhydrylamine thereby is almost quantitative.[24)]

The reduction of oximes with Urushibara nickel catalysts can proceed at ordinary temperature and pressure. Table 8–12 illustrates such a reduction of cyclohexanone oxime. Reduction at ordinary temperature and pressure, however, requires a longer reaction time, just as with nitriles; thus high temperature and pressure are recommended.

8. 1. 7. Reduction of Hydroxylamine

Information is available on the catalytic reduction of *N*-benzylhydroxylamine.[24] The reduction of 0.1 mole (12.1 g) of this material in the presence of U–Ni–B (containing 0.5 g of nickel) at 73°C and under an initial hydrogen pressure of 36 kg/cm^2 terminates in 55 minutes, and gives an 82% yield of benzylamine and 5% of dibenzylamine.

A mechanism was proposed in the past, in which *N*-benzylhydroxylamine was thought to be an intermediate in the reduction of benzaldoxime to benzylamine and dibenzylamine. This mechanism has been rejected because the formation of secondary amine is very small in the above experiment (cf. Table 8–15).

8. 1. 8. Reduction of Epoxides

In the presence of Raney nickel or platinum oxide, 1,2-epoxides are easily reduced to the corresponding alcohols. Newman *et al.**1) examined the direction of hydrogenolyses in many unsymmetrically substituted ethylene oxides in the presence of Raney nickel.

Characteristics of the hydrogenolyses of epoxides in the presence of U–Ni–A are also available, especially for styrene oxide and β-methylstyrene oxide. Table 8–17 clearly demonstrates that fission occurs between the α-carbon and oxygen, thereby giving phenethyl alcohol and 1-phenyl-2-propanol, respectively. This result is in agreement with that for Raney nickel.

8. 1. 9. Reduction of Benzyl Halides

Grigorovskiĭ and Fedorov*2) investigated the hydrogenolysis of benzyl chloride in the presence of Raney nickel. They observed that toluene was the main product, but that a small amount of bibenzyl was also formed on account of a Wurtz type condensation reaction.

H. Isogai[28] reexamined the reaction, and confirmed the result of Grigorovskiĭ and Fedorov; he studied the same reaction also in the presence of U–Ni–B. He showed that in the presence of U–Ni–B, the main product is toluene, but that the formation of bibenzyl is somewhat larger and a greater amount of catalyst tends to increase the

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*1) M. S. Newman, G. Underwood, and M. Renoll, *J. Amer. Chem. Soc.*, **71**, 3362 (1949).

*2) R. M. Grigorovskiĭ and V. S. Fedorov, *Zhur. Priklad. Khim.*, **21**, 529 (1948); *Chem. Abst.*, **43**, 646 (1949).

Table 8–17. Reduction of 1,2–Epoxides under High Pressure

Compound	Amount of sample		Catalyst	Nickel content (g)	Solvent (cyclohexane) (ml)	Initial pressure (kg/cm^2)	Temperature (°C)	Time (min)	Product	Yield (%)
	mole	g								
styrene oxide	0.14	16.8	U–Ni–A	1.5	50	46	49–65	60	phenethyl alcohol	68
β–methylstyrene oxide	0.149	20	U–Ni–A	3	60	50	70	60	1–phenyl–2–propanol	72

Table 8–18. Reduction of Benzyl Halides under Atmospheric Pressure and at Room Temperature

Compound	Amount of sample		Catalyst	Weight of catalyst[a] (g)	Solvent (methanol) (g)	Product (g)		Reference
	mole	g				toluene	bibenzyl	
benzyl chloride	0.05	6.3	U–Ni–B	5	50	2.8	0.5	28)
„	„	„	„	10	„	2.7	0.8	„
„	„	„	„	20	„	2.0	1.3	„
„	„	„	„	30	„	1.9	1.5	„
benzyl bromide	0.05	8.5	„	5	„	0.2	2.0	„

[a] Weight of wet catalyst. The nickel content of 10 g of the wet catalyst is estimated to be 0.7–0.9 g.

Table 8–19. Reduction of Steroids under Atmospheric

Compound	Weight of sample (g)	Catalyst (U-Ni-B)		Solvent (ml)	
		Method of preparation[a]	Nickel content (g)		
Unsaturated Alcohols					
ergosterol	0.3	Prep. 3[b]	0.5	ethanol	80
ergosteryl acetate	0.05	„	„	ethanol[c]	80
Saturated Ketones					
5α-cholestan-3-one	0.3	Prep. 1	0.45	ethanol	30
5β-cholestan-3-one	0.3	„	„	„	30
3β-hydroxy-5α-cholestan-6-one	0.3	„	„	„	40
3β-hydroxy-5α-cholestan-7-one	0.3	„	„	„	40
dehydrocholic acid	0.3	„	„	alkaline water	
Unsaturated Ketones					
cholest-4-en-3-one	0.3	Prep. 1	0.45	ethanol	30
7-oxocholesteryl acetate	0.3	„	„	„	40
Unsaturated Nitro Compound					
6-nitrocholesteryl acetate	0.3	Prep. 1	0.45	ethanol	40

[a] See Chapter 4.

[b] A catalyst prepared by Preparation 3 was further treated with NaCl solution. It was washed well with water and then with ethanol.

formation of the latter at the expense of the former (Table 8–18).

The reduction of benzyl bromide gives mainly bibenzyl, and the amount of toluene produced is very small; the same result is obtained with Raney nickel.

8. 1. 10. Reduction of Steroids

The discovery of the Urushibara catalysts was due to the exploitation of a novel method for the reduction of estrone. Hence, we shall begin with some of the earlier methods which are now of historical interest. The reduction of estrone, established in this early period,[3] involves

Pressure in the Presence of U–Ni–B

Temperature (°C)	Time (min)	Amount of absorbed hydrogen (mole)	Product	Configuration of the product	Reference
22	40	1.5	5,6-dihydroergosterol	5α	6)
19	30	—	5,6-dihydroergosteryl acetate	5α	6)
10–15	10	1	5α-cholestan-3-ol	3α 10% 3β 90%	7)
„	10	1	5β-cholestan-3-ol	3α 58% 3β 42%	„
„	60	1	5α-cholestane-3β,6β-diol	6β	„
„	70	1	5α-cholestane-3β,7-diol	7α 50% 7β 50%	„
„	15	1	3α-hydroxy-7,12-dioxocholanoic acid	3α	„
10–15	10	2	5α-cholestan-3-ol 5β-cholestan-3-ol	3α 5% 3β 50% 3α 25% 3β 20%	7)
„	15	1	7-oxo-5α-cholestanyl acetate	5α	„
10–15	30	2	6-hydroxyiminocholestanyl acetate	5α	7)

[c] A small amount of ether was added.

the addition of precipitated nickel to an alkaline solution of estrone, to which aluminum chips are then added to liberate hydrogen. It has subsequently developed that precipitated copper, in place of the precipitated nickel, also gives estradiol-17β in a good yield.[27] The modified method is the following:

Zinc dust is added to 5 g of $CuSO_4 \cdot 5H_2O$ dissolved in 100 ml of water, until the color of the copper(II) ion disappears. The precipitated copper is washed with water and added to 50 mg of estrone dissolved in 65 ml of 10% potassium hydroxide solution. The solution is heated on a water bath with stirring, while 3 g of aluminum

chips are added in small portions over a period of 10 hours. When the reaction is over, solid matter is filtered off, and the filtrate, made acid with hydrochloric acid, is extracted with ether. From the extract, 40 mg of estradiol-17β is obtained. Copper(II) chloride or copper(II) acetate may be used instead of copper(II) sulfate with almost the same result.

A further modification consists in the use of zinc dust in place of aluminum chips. Zinc dust (4 g) is added in one portion to 50 mg of estrone dissolved in 65 ml of 10% potassium hydroxide solution. The solution is heated on a water bath with stirring and the precipitated copper, prepared from 5 g of copper(II) sulfate crystals and zinc dust, is added in small portions over a period of 10 hours. The yield of estradiol-17β is the same as in the former method.

The precipitated nickel showed catalytic activity when it was treated with alkali, and thus a new catalyst, U–Ni–B, was discovered. Since then, this catalyst has been employed for a wide range of reductions, including the reduction of steroids. Table 8–19 illustrates the reduction of a number of steroids in the presence of U–Ni–B.

It has been shown*1) that ergosterol undergoes partial hydrogenation at its $\Delta^{5,7}$-conjugated double bonds in the presence of Raney nickel, and gives a Δ^{7}-steroid. This is also the case with U–Ni–B, in which 5,6-dihydroergosterol is obtained in an 80% yield with the uptake of hydrogen in slight excess, provided the catalyst is treated in advance with sodium chloride solution to remove even a trace of alkali.[6] The partial reduction of ergosteryl acetate also proceeds in the presence of U–Ni–B, and gives a 5,6-dihydro-compound.

Steroid ketones easily absorb one mole of hydrogen and are reduced to the corresponding alcohols.[7] The configurations of the hydroxyl groups formed differ according to the kind of starting materials, but do not differ according to the catalyst. Insofar as experimantal evidence is available, Raney nickel and Urushibara nickel give the same results with regard to stereochemical relations. For example, 3β-hydroxy-5α-chlolestan-6-one is reduced quantitatively to 5α-cholestane-3β,6β-diol in the presence of either catalyst.

Cholest-4-en-3-one is reduced to a mixture of four stereoisomeric alcohols. In the presence of U–Ni–B, the main product is 5α-cholestan-

*1) G. D. Laubach and K. J. Brunings, *J. Amer. Chem. Soc.*, **74**, 705 (1952); W. V. Ruyle, E. M. Chamberlain, J. M. Chemerda, G. E. Sita, L. M. Aliminosa, and R. L. Erickson, *ibid.*, **74**, 5929 (1952); R. C. Anderson, R. Stevenson, and F. S. Spring, *J. Chem. Soc.*, **1952**, 2901.

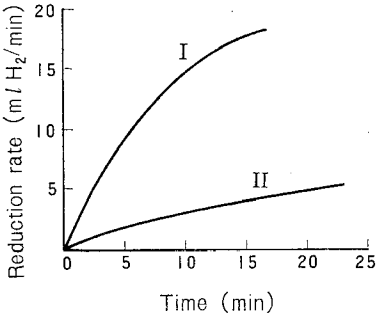


Fig. 8–2. Reduction of Dehydrocholic Acid in the Presence of U–Ni–B

Sample: 0.3 g
Catalyst: U–Ni–B containing 0.45 g of Ni
I: in alkaline aqueous solution
II: in neutral ethanol solution

3β-ol, and Raney nickel gives the same result. However, the results with palladium*1) *2) and platinum*2) are somewhat different.

The reduction of dehydrocholic acid by U–Ni–B proceeds very slowly and incompletely in an ethanol solution (Fig. 8–2).[7] In an alkaline aqueous solution, reduction takes place rapidly with the uptake of one mole of hydrogen, and then reduction stops. The product is a 3α-hydroxy compound, only one carbonyl group (3-position) among three (3-, 7- and 12-) being reduced.

In the reduction of 7-oxocholesteryl acetate in ethanol by U–Ni–B, the absorption of the first mole of hydrogen is comparatively rapid, but this is followed by a sudden fall in the rate. Interruption of the reduction at this tage allows 7-oxo-5α-cholestanyl acetate to be isolated. The yield is about 70%.

The reduction of 6-nitrocholesteryl acetate in ethanol proceeds in the presence of U–Ni–B with the uptake of two moles of hydrogen in about 30 minutes. The reduction stops at this stage and gives an oxime in a 70% yield, which is identified as the oxime of 6-oxo-5α-cholestanyl acetate. Raney nickel is also applicable to this reduction, with almost the same result.

*1) H. Grasshof, *Z. Physiol. Chem.*, **223**, 349 (1934).
*2) L. Ruzicka, H. Brüngger, E. Eichenberger, and J. Meyer, *Helv. Chim. Acta*, **17**, 1407 (1934).

8. 2. Hydrogenation with Heavy Hydrogen

Catalytic reduction with Urushibara nickel catalysts can be applied to the synthesis of organic compounds containing deuterium or tritium. For this purpose, U–Ni–A is prefered because of its smaller bulk, which minimizes the loss of the expensive heavy hydrogen. It was found that the Urushibara nickel catalyst is preferable even to Raney nickel, as the former contains a lesser amount of adsorbed hydrogen.

8. 2. 1. Deuteration

T. Morita and H. Kawashima have tried to synthesize deuterated 1-phenylethanol, a source material of styrene-α,β,β-d_3, by the catalytic deuteration of acetophenone-ω,ω,ω-d_3:

$$C_6H_5COCD_3 + D_2 \xrightarrow{\text{U-Ni-A}} C_6H_5{-}\underset{\displaystyle OD}{\underset{|}{CD}}{-}CD_3$$

Deuterium was obtained by the electrolysis of heavy water of 99.80% purity in the apparatus shown in Fig. 8–3. About 10 ml of heavy water, made alkaline with sodium amalgam, was electrolyzed with nickel electrodes in a V-tube (A). The vessel had a small dip at the bottom to provide a mercury reservoir. The electric current was

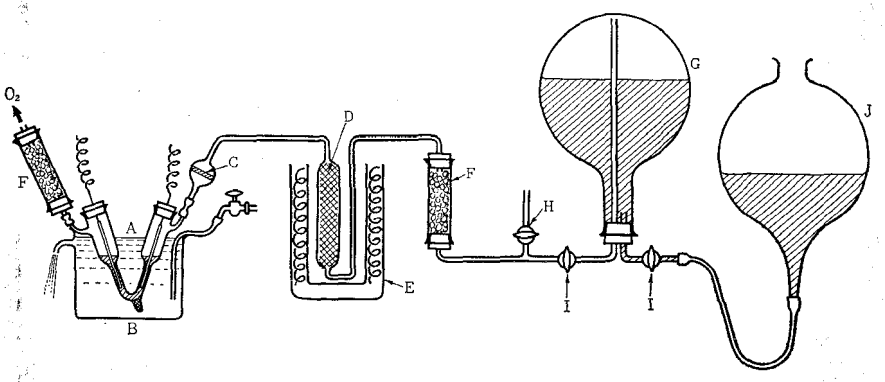


Fig. 8–3. Deuterium Generator and Collector

A, Electrolyzer; B, Cooling bath; C, Sintered glass filter (for splash-board); D, Glass tube filled with copper wire; E, Heater; F, Calcium chloride tube; G, Gas holder; H, Vent; J, Reservoir (liquid paraffin); I, Stopcocks

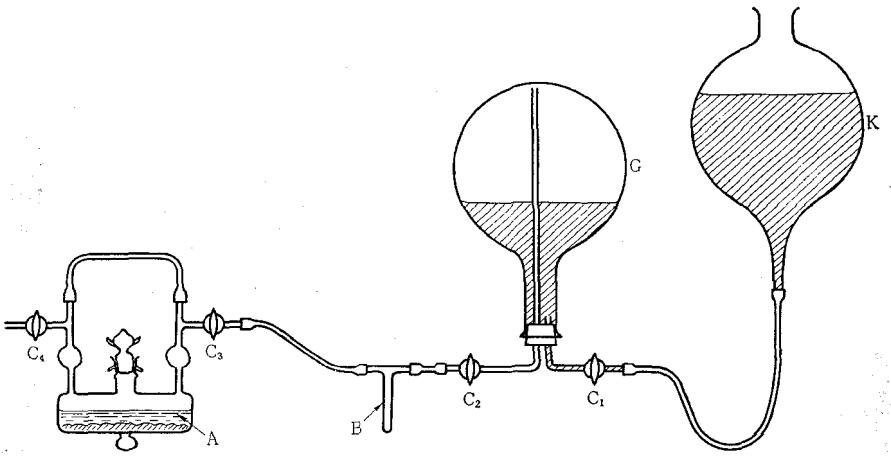


Fig. 8–4. Deuteration Apparatus

A, Reactor; B, Liquid paraffin trap; C_1, C_2, C_3, C_4, Stopcocks; G, Gas holder; K, Reservoir (liquid paraffin)

adjusted to about 0.8 A and the whole vessel was cooled with running water to prevent overheating. The liberated oxygen was allowed to escape into the air. Deuterium was passed through copper wire at 400°C (D) to eliminate any contaminating oxygen, dried over calcium chloride, and collected on liquid paraffin in a 5-*l* flask (G), which was graduated by a rough calibration and used as a gas holder. It was confirmed that no hydrogen exchange reaction occurred through the contact between the liquid paraffin and deuterium.

Catalytic deuteration was effected with the apparatus shown in Fig. 8–4. A is the usual rocking reactor for catalytic reduction under ordinary pressure. Deuterium was supplied from the gas holder by adjusting the flow of liquid paraffin from the reservoir (K). The out let of the gas holder was provided with a small trap (B) to prevent accidental contamination of the reactor with liquid paraffin.

The catalyst, U–Ni–A, which was prepared by the standard method so as to contain about 2.5 g of nickel, was washed first with ethanol to replace water, and then several times with small amounts of the sample, acetophenone-ω,ω,ω-d_3, so that the remaining ethanol could be replaced as completely as possible. The sample, acetophenone-ω,ω,ω-d_3, prepared from acetophenone by virtue of a deuterium exchange reaction, was found to be of 98.1% purity. The catalyst

was transferred to the reactor, and 25 g of the sample was added. Stopcocks C_3 and C_4 were opened and the reactor was evacuated through C_4. Stopcock C_4 was then closed and the reactor was filled with deuterium through stopcocks C_1 and C_2. The process was repeated three times in order to expel air from the reactor as completely as possible. The reactor was then shaken vigorously while C_4 was closed, and deuteration was allowed to begin. The reactor was heated with a 500 W infrared lamp, which was placed about 50 cm away. The sample absorbed, over a period of 9 hours, 4.7 *l* of deuterium, which was nearly the theoretical amount, and gave 1-phenylethanol in a good yield. The somewhat longer time for deuteration, as compared with ordinary hydrogenation, is apparently due to the inevitable contact of the catalyst with air during the complicated washing and replacing processes, which would have caused a decrease of activity.

8. 2. 2. Tritiation

M. Muramatsu, *et al.*[35) 43)] described the catalytic tritiation of oleic acid and 2-dodecenoic acid to stearic acid and lauric acid. It was intended that the products should be labeled with tritium at particular sites, and should possess high purity from both the physicochemical and radiochemical points of view as samples for physicochemical use. To obtain starting material, oleic acid of extremely high purity was rectified and recrystallized by both the Pb-salt and Li-salt methods to remove homologous fatty acids and other impurities, such as linoleic or linolenic acids, and then again rectified. The sample was tritiated in the presence of U–Ni–A to give stearic-9,10-t_2 acid.

$$\underset{\text{oleic acid}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH} + {}^3H_2 \xrightarrow{\text{U-Ni-A}} \underset{\text{stearic-9,10-}t_2\text{ acid}}{CH_3(CH_2)_7CH^3H\text{-}CH^3H(CH_2)_7COOH}$$

2-Dodecenoic acid was obtained by a somewhat complicated method. Highly purified 1-dodecanol was oxidized to lauric acid, which, after rectification, was heated with bromine in the presence of phosphorus trichloride to give 2-bromododecanoic acid. The latter was refluxed with potassium iodide in ethanol to yield 2-iodododecanoic acid, which was again refluxed with ethanolic potash to give 2-dodecenoic acid. The raw 2-dodecenoic acid was purified by both the Pb-salt and Li-salt methods, and rectified. Lauric-2,3-t_2 acid was obtained by the tritiation of pure 2-dodecenoic acid in the presence of U–Ni–A.

$$\underset{\text{2-dodecenoic acid}}{CH_3(CH_2)_8CH{=}CHCOOH} + {}^3H_2 \xrightarrow{\text{U-Ni-A}} \underset{\text{lauric-2,3-}t_2\text{ acid}}{CH_3(CH_2)_8CH^3H\text{-}CH^3HCOOH}$$

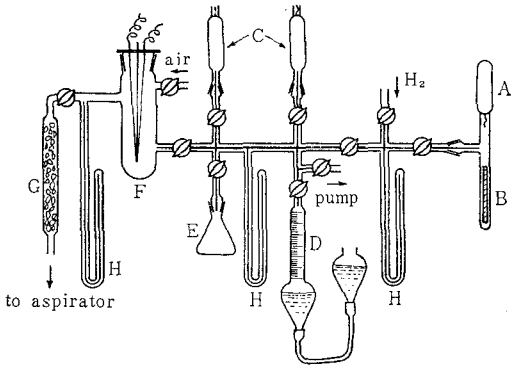


Fig. 8–5. Tritiation Apparatus

A, Tritium ampoule; B, Breaker; C, Ampoule for reservation of tritium; D, Graduated Toepler; E, Reaction flask; F, Combustion bulb; G, Calcium chloride tube; H, Manometer.

A solvent for tritiation should have the following properties: It should have no readily exchangeable hydrogen and should dissolve fatty acids well, but should not dissolve hydrogen well. Its boiling point should not be very low. With these criteria in mind, dioxane was employed as a solvent. It was freed from contaminating glycol and acetal by treatment with silver oxide, and then dried and distilled.

Tritium of 96% purity ($^3H/(^3H+H)$) was provided from an ampoule (708 mc), from which about 200 mc was used for the tritiation of oleic acid, and another 240 mc portion was used for the tritiation of 2-dodecenoic acid.

The apparatus for tritiation, shown in Fig. 8–5, was essentially the same as that reported by Williams and Ronzio.*1) A is a sealed ampoule of tritium and B is a breaker. The reaction flask E contained 0.830 g of oleic acid, 10 ml of dioxane and U–Ni–A corresponding to 0.3 g of nickel. The apparatus was evacuated and the remaining air was removed by flushing several times with ordinary hydrogen. When complete evacuation was attained, A and B were turned upside down to break the ampoule and part of the tritium was allowed to flow into the other ampoules (C). These were subsequently isolated from the remainder of the apparatus by sealing off at their necks. These ampoules were provided to save part of the tritium for use in succeeding experiments. The first experiment was carried out with the tritium

*1) D. L. Williams and A. R. Ronzio, *J. Amer. Chem. Soc.*, **72**, 5787 (1950).

remaining in A (about 200 mc). The tritium was transferred into a graduated Toepler (D) as completely as possible, and a new portion of purified hydrogen was introduced into A, where it was mixed with the remaining tritium and then transferred to D. The process was repeated several times. D now contained 10–30 ml of hydrogen containing tritium, which was used to hydrogenate the sample in E.

Hydrogenation was initiated by connecting the Toepler D and reaction flask E, and stirring the reactant solution vigorously with a magnetic stirrer. To facilitate the reaction, the reactor E was heated slightly from the outside with an infrared lamp. The rate of hydrogen uptake was measured by means of the graduations on D, and hydrogen was repeatedly supplied from A as soon as it was exhausted in D.

The reaction terminated when the sample absorbed just one mole of hydrogen, which corresponded to the complete saturation of oleic acid. The rate of hydrogen uptake is illustrated in Fig. 8–6.

The remaining radioactive tritium was disposed of as follows: The mixture of hydrogen and tritium remaining in D and E was led to a combustion bulb F, where it was mixed with a proper amount of air and ignited to form tritium oxide. It was then led through a calcium chloride tube G under suction for discarding.

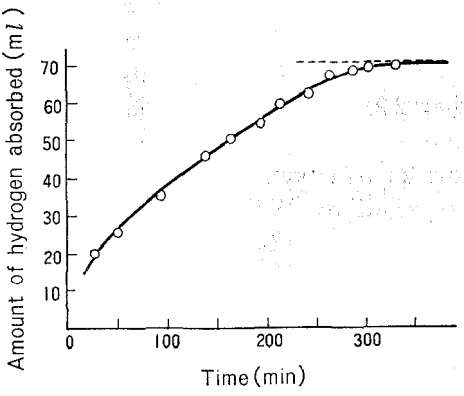


Fig. 8–6. Rate of Absorption of Hydrogen Containing Tritium by Oleic Acid

Oleic acid: 0.830 g
$^3H_2$: 200 mc
Catalyst: U–Ni–A, containing 0.3 g of Ni
Solvent: dioxane, 10 ml
------: calculated value of saturation

The tritiation product was carefully evaporated to dryness, treated with hydrochloric acid to dissolve away the catalyst metal, and extracted with ether. Solid matter obtained from the extract was dissolved in methanol, which was then distilled off after one hour of standing. This process was repeated several times, until the tritium substituted at the carboxylic group was diluted with hydrogen by a factor of perhaps 10^{-15} by virtue of the exchange reaction with methanol. The product was then recrystallized several times from ether.

The same method was applied to obtain lauric acid. The rate of tritiation of 1.66 g of 2-dodecenoic acid in 10 ml of dioxane with hydrogen containing ca. 240 mc of tritium in the presence of U–Ni–A (corresponding to 0.5 g of nickel) is shown in Fig. 8–7. The reaction terminated when one mole of hydrogen was absorbed, and gave pure lauric acid by the same treatment as for oleic acid.

Definite amounts of the tritium-labeled stearic and lauric acids thus obtained were dissolved in benzene and spread to make thin films. Their radioactivities were measured with a 2π-gas flow counter. Radioactive yields of the tritiation products were found to be 72–54% for stearic acid and 71.2% for lauric acid. It was suggested that the comparatively low yields were attributable to the exchange which might have taken place between tritium and either the hydrogen originally

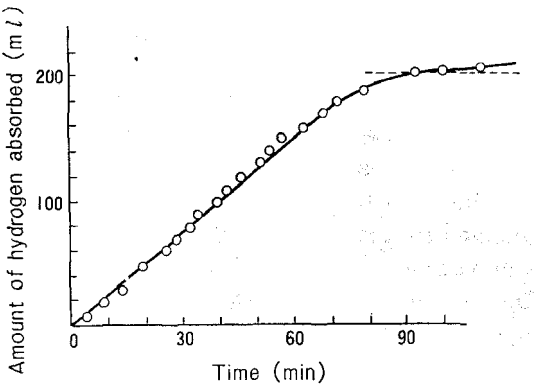


Fig. 8–7. Rate of Absorption of Hydrogen Containing Tritium by 2-Dodecenoic Acid

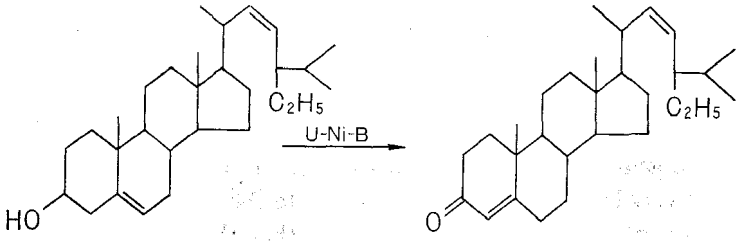
2-Dodecenoic acid: 1.66 g
$^3H_2$: ca. 240 mc
Catalyst: U–Ni–A, containing 0.5 g of Ni
Solvent: dioxane, 10 ml
----: calculated value of saturation

adsorbed on the catalyst (9–10 ml) or the hydrogen of the carboxyl group.

8.3. Dehydrogenation

Proper reaction conditions allow a hydrogenation catalyst to act as a dehydrogenation catalyst. For example, E. C. Kleiderer and E. C. Kornfeld*[1] obtained cholestenone and cholestanone in an 80% yield by the dehydrogenation of cholesterol and dihydrocholesterol in the presence of Raney nickel, using cyclohexanone as a hydrogen acceptor.

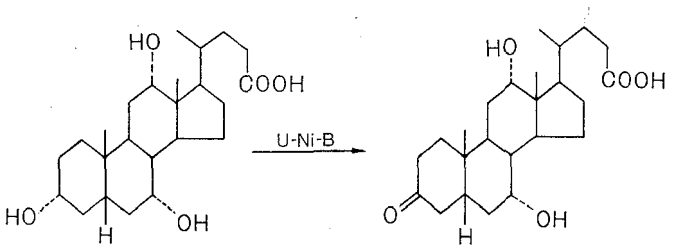
Urushibara catalysts also provide several examples. In the presence of U–Ni–B, stigmasterol and cholic acid undergo dehydrogenation to give the corresponding 3-keto compounds.



U–Ni–B prepared from 8 g of nickel chloride crystals, $NiCl_2 \cdot 6H_2O$, by way of Preparation 3, Chapter 4, was repeatedly washed with toluene to remove water, and transferred with a small amount of the solvent to a three-necked flask provided with a Dean-Stark trap and a sealed stirrer. The flask contained 30 ml of dried toluene, 15 ml of purified cyclohexanone, and 1 g of stigmasterol. The mixture was refluxed for 25 hours with thorough stirring. The mixture was then allowed to cool and the catalyst was centrifuged out. The solvent was distilled off in vacuo and the solid residue was recrystallized from ethanol. The product was stigmasta-4,22-dien-3-one, needles, m.p. 124–126°C. The yield was 310 mg. It was identified by melting with an authentic sample.

The same method was applied to the dehydrogenation of cholic acid. U–Ni–B containing 1.8 g of nickel was washed well with toluene and transferred to a three-necked flask containing 30 ml of toluene and 1 g of cholic acid dissolved in 15 ml of cyclohexanone. The mixture was refluxed for 25 hours. After cooling, the catalyst was filtered off

*1) E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).



and the filtrate was washed with petroleum ether and distilled with steam. The residue was extracted with petroleum ether and dried over anhydrous sodium sulfate. Solid matter from the extract was recrystallized from aqueous ethanol. The product was 7α,12α-dihydroxy-3-oxo-5β-cholanoic acid, needles, m.p. 183–184°C. The yield was 400 mg.

This information was obtained from experiments carried out in an early period after the discovery of the Urushibara nickel catalyst. Therefore, the low yields (30–40%) are attributed to the low activity of the catalyst, and a high yield comparable to that obtained with Raney nickel can perhaps be expected with an Urushibara catalyst of improved activity.

8. 4. Reductive Desulfurization

J. Bougault, E. Cattelain, and P. Chabrier*[1] found that many organic sulfur compounds are desulfurized to hydrocarbons by hydrogen adsorbed on Raney nickel. They showed that when sulfur compounds, such as thiols, sulfides, disulfides, and thioacetals, were heated with Raney nickel in aqueous or alcoholic media, the sulfur-containing groups were eliminated reductively, thereby giving the corresponding hydrocarbons in good yields; the eliminated sulfur combined with the catalyst to give nickel sulfide. The method was soon applied to many other sulfur compounds and gave good results. Especially in the field of steroid chemistry, the method is particularly useful because the reduction of a keto group to methylene can be easily attained through conversion to thioacetal, followed by reductive desulfurization in the presence of Raney nickel.

*1) J. Bougault, E. Cattelain and P. Chabrier, *Compt. Rend.*, **208**, 657 (1939); *Bull. Soc. Chim.*, **7**, 781 (1940); *Chem. Abst.*, **33**, 4580 (1939); **36**, 2198 (1942).

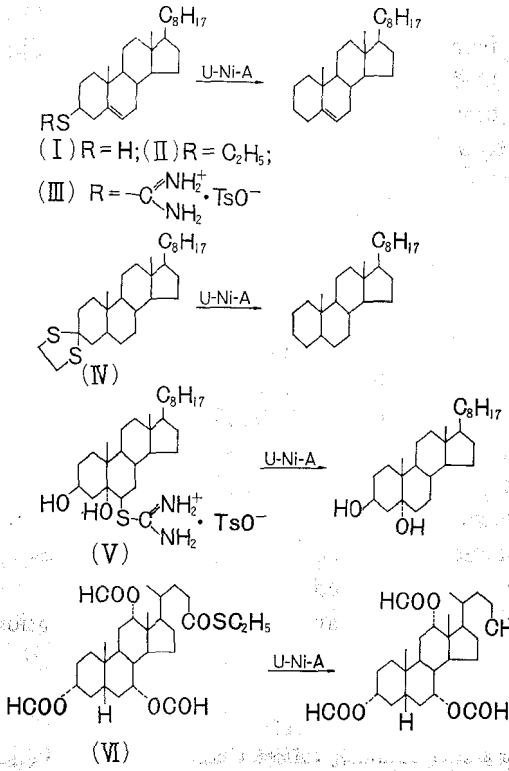
Table 8–20. Reductive Desulfurization of Steroids in the Presence of U–Ni–A

Compound	Amount of sample (mg)	Nickel content of catalyst (g)	Solvent (ml)	Refluxing time (hr)	Product	Yield (%)
cholest–5–ene–3β–thiol (I)	300	2.5	dioxane 30	8	cholest–5–ene	54
„	100	1	ethanol 80	1	„	90
3β–ethylthiocholest–5–ene (II)	210	3	dioxane 30	14	cholest–5–ene	72
„	100	1	ethanol 80	5	„	68
cholesteryl disulfide	200	3	dioxane 30	14	cholest–5–ene	68
„	100	1	ethanol 80	5	„	75
S–cholesterylthiouronium *p*–tosylate (III)	305	3	dioxane 30	14	cholest–5–ene	48
„	314	3	ethanol 50	2	„	61
„	168	1.5	ethanol 40	1	„	42
„	100	1	ethanol 80	1	„	100
3,3–ethylenedithio–5α–cholestane (IV)	198	2.5	dioxane 40	14	5α–cholestane	100
S–(3β,5α–dihydroxycholestan–6–yl)–thiouronium *p*–tosylate (V)	100	1	ethanol 80	1	cholestane–3β,5α–diol	93
S–ethyl 3α,7α,12α–triformyloxy–5β–thiocholanoate (VI)	100	1	aqueous acetone	1	3α,7α,12α–triformyloxy–5β–cholestan–24–al	—

The Urushibara nickel catalysts have many characteristics very like those of Raney nickel in hydrogenation, and can replace the latter without any modifications in processes or yields. Moreover, the Urushibara nickel catalysts, just like the Raney nickel catalysts, contain adsorbed hydrogen, as their preparation involves a stage where a large amount of hydrogen is liberated. The amount of hydrogen adsorbed on U–Ni–BA has been determined by T. Yamanaka *et al.*[25] to be somewhat less than that on Raney nickel, but still not negligible. Therefore, reductive desulfurization of various sulfur compounds in the presence of the Urushibara nickel catalysts was investigated, and proved practical.

Table 8–20 provides several examples of reductive desulfurization in the presence of U–Ni–A for sulfur-containing steroides. When the samples were refluxed with the catalyst in ethanol or dioxane, they underwent desulfurization, giving the corresponding hydrocarbons.

U–Ni–B was found to be useless, as it failed to give good results.



It was found that reductive desulfurization in the presence of U–Ni–A applies as well to the diethyl thioacetals of benzaldehyde, acetophenone, benzophenone etc. They are readily desulfurized when refluxed with U–Ni–A in ethanol, but information with regard to the yields of products or other aspects is lacking.

8. 5. Reductive Alkylation

It sometimes happens that the catalytic reduction of aromatic amines in alcohol is accompanied by alkylation at the amino group.*1) Such *N*-alkylation is often encountered in catalytic reduction with an Urushibara nickel catalyst. For example, it was reported[31] that *N*-ethylcyclohexylamine was obtained as the main product when aniline was reduced in ethanol in the presence of U–Ni–BA at 150–200°C and under an initial pressure of hydrogen of 75–95 kg/cm² (Table 8–4). The same reduction in cyclohexane, in place of ethanol, gave only cyclohexylamine and dicyclohexylamine.

Another example of reductive alkylation is provided by the preparation of Metol from *p*-aminophenol and formalin. This experiment, which employs U–Ni–A prepared on a large scale in a specially designed apparatus, was carried out to provide a basis for the industrial application of Urushibara nickel catalysts.

To 200 g of *p*-aminophenol dissolved in 2 *l* of methanol were added 80 g of 50% sodium hydroxide solution, 200 g of formalin (35%) and 50 g of U–Ni–A, and the whole mixture was heated gently to boiling in a cylindrical steel reactor provided with a reflux condenser, while hydrogen was allowed to pass through at a rate of 1.0 *l*/min. The reaction terminated in 70 minutes after 25 *l* of hydrogen had been absorbed. A considerable amount of tarry matter was formed. The mixture was neutralized with 30% sulfuric acid, and the catalyst and the tarry product were filtered off. The filtrate was evaporated in a hydrogen atmosphere, and the remaining violet crystals recrystallized from methanol with active charcoal. *p*-Methylaminophenol sulfate (Metol) was obtained as white needles. The yield was 73 g, 30% of the amount of *p*-aminophenol used.

The low yield would appear to be due to the formation of phenolic resin, which is favored by the presence of alkali. As the latter is also

*1) H. I. Cramer and H. Adkins, *J. Amer. Chem. Soc.*, **52**, 4354 (1930).

indispensable for the formation of Metol, further investigation regarding reduction conditions is required to improve the yield.

8. 6. Reductive Condensation

The catalytic reduction of benzyl chloride treated in Section 8. 1. 9 provides a good example of reductive condensation; we shall describe the subject more fully in what follows. As we have seen, certain aspects of the reduction are different depending on the catalyst employed. In the presence of Raney nickel, the main product is toluene and a very small amount of bibenzyl is formed as a by-product.*1) The same products are obtained with U–Ni–B, but the formation of bibenzyl is greatly increased.

H. Isogai[28] investigated the Wurtz type reductive condensation of this material in the presence of both catalysts, showing that the formation of bibenzyl in the presence of U–Ni–B increases with the amount of catalyst used (Fig. 8–8 (a)), in contrast to the case with Raney nickel W–4, where the amount of bibenzyl did not change remarkably, irrespective of the amount of catalyst employed (Fig. 8–8 (b)). Information was obtained from experiments in which 6.3 g (0.05 mole) of benzyl chloride dissolved in 50 ml of methanol was mixed with 2 g (0.05 mole) of sodium hydroxide and a varying amount of catalyst, and shaken with hydrogen at ordinary temperature and pressure. Pertinent data may be found in Table 8–18 above.

A considerable amount of hydrogen is adsorbed on either Raney nickel or Urushibara nickel, and hydrogenation can be effected by the adsorbed hydrogen alone. Yields of products, when 6.3 g (0.05 mole) of benzyl chloride in 50 ml of methanol was refluxed with stirring for 3 hours with varying amounts of either U–Ni–B or Raney nickel, are illustrated in Fig. 8–8 (c) and (d), respectively. We see that toluene is still the main product in the case of Raney nickel, but that the yield of bibenzyl increases when the amount of catalyst is small. In the case of Urushibara nickel, however, most of the benzyl chloride is converted to bibenzyl, and scarcely any toluene is formed.*2)

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*1) R. M. Grigorovskiĭ and V. S. Fedrov, *Zhur. Priklad. Khim.*, **21**, 529 (1948), *Chem. Abst.*, **43**, 646 (1949).

*2) K. Watanabe[29] reported that almost pure bibenzyl was obtained in a 71% yield when 10 g of benzyl chloride in 70 ml of ethanol was mixed with U–Ni–B (containing 4 g of nickel) and refluxed for 6 hours.

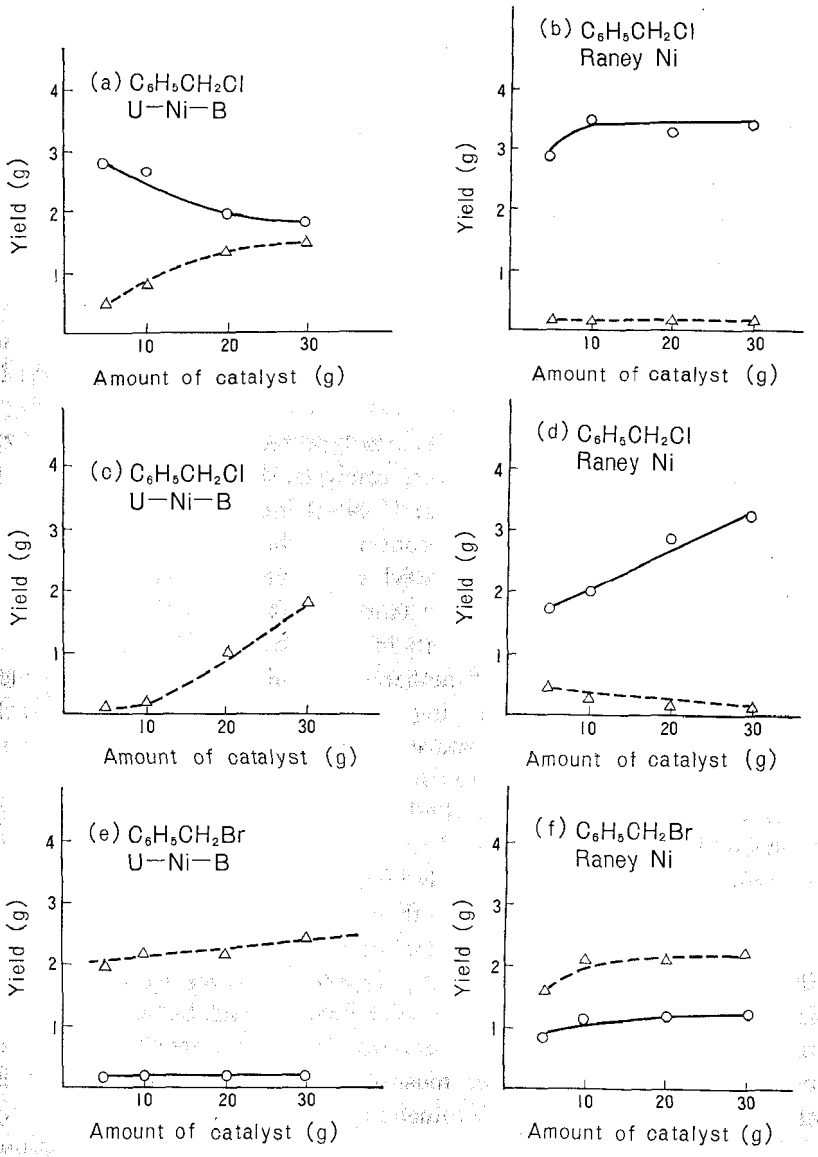

Fig. 8–8. Reduction of Benzyl Halides in the Presence of U–Ni–B or Raney Nickel

(a), (b), (e), (f): reduction with hydrogen gas
(c), (d): reduction with hydrogen originally adsorbed on the catalyst
○ toluene; △ bibenzyl

It was found that, even in the presence of Raney nickel, bibenzyl was the only product from benzyl chloride, provided the catalyst was heated beforehand at 150°C for one hour in a nitrogen atmosphere of 2 mmHg to remove the adsorbed hydrogen.

The same experiments with benzyl bromide gave somewhat different results (Fig. 8–8 (e) and (f)). Here 8.5 g (0.05 mole) of benzyl bromide was dissolved in 50 ml of methanol and shaken with hydrogen in the presence of either U–Ni–B or Raney nickel. Bibenzyl is always the main product, even with Raney nickel. With U–Ni–B, the formation of toluene is quite small.

8.7. Hydration of Nitriles to Amides

K. Watanabe[29] tried to use Urushibara catalysts for other than usual reactions, and found that they were able to effect the hydration of aromatic nitriles to amides with considerable yields if the former were refluxed with water in their presence. The method has the advantage that the reaction may proceed in a neutral medium, so that no drastic conditions, such as the use of acid or alkali, are necessary. The reaction usually stops at the amide stage and scarcely hydrolysis to acid takes place. It has been confirmed that the amides themselves will not be hydrolyzed to acid even in the presence of freshly prepared catalyst. However, the hydration of nitrile is sometimes accompanied by the hydrogenation of a sample to a lesser extent on account of the adsorbed hydrogen, thereby giving a very small amount of amine as a by-product. We present in the following the hydration of benzonitrile with U–Ni–B for illustrative purposes.

U–Ni–B, containing 4 g of nickel, was placed in a 200 ml round-bottomed flask containing 5 g of benzonitrile and 80 ml of water. The flask was fitted with a reflux condenser and the contents were refluxed for some 8 hours, during which the benzonitrile on the surface of the water gradually disappeared. When the reaction was over, the mixture was filtered while hot and the filtrate was evaporated on a boiling water bath. Benzamide of considerable purity was obtained as white crystals. The yield was 78%.

It is perhaps worth noting that the preparation of a catalyst to be used for hydration requires no particular care, such as is always necessary for the preparation of hydrogenating catalysts; for example, the use of purified water or the exclusion of air during preparation.

Hydration may also proceed in other solvents such as ethanol,

Table 8–21. Hydration of Benzonitrile to Benzamide in Various Solvents in the Presence of U–Ni–B

Weight of benzonitrile (g)	Nickel content of U–Ni–B (g)	Solvent (ml)	Refluxing time (hr)	Yield of benzamide (g)	Recovered benzonitrile (g)	Formation of benzylamine (hydrochloride, g)
5	2	water 80	9	57	+	–
5	4	water 80	11	73	–	–
5	4	water 80	8	78	–	–
15	8	water 150	10	74	–	–
5	4	ethanol 60	9	11	–	4
5	8	ethanol 100	2.5	19	0.6	2
10	8	ethanol 100	8	19	1	3.6
10	4	methanol 100	10	12	4	+
5	4	1–butanol 80	4	7	–	3.4
10	8	dioxane 100	12	34	+	1.5

Table 8–22. Hydration of Benzonitrile to Benzamide with Various Catalysts

Catalyst	Nickel or copper content (g)	Weight of benzonitrile (g)	Solvent (ml)		Refluxing time (hr)	Yield of benzamide (%)	Recovered benzonitrile (g)
U-Ni-B	4	5	water	80	8	78	–
U-Ni-A	3	3	water	80	8	71.5	–
U-Ni-A	3	5	ethanol	60	8	5	1.6
U-Ni-BA	4	5	water	80	9	34.5	1.4
U-Ni-BA	4	5	ethanol	80	9	5	1.7
U-Cu	4	5	water	100	8	24	–
U-Cu	4	5	ethanol	60	8	+	0.8
Raney Ni	4	10	water	100	8	65	–
Raney Ni	4	10	ethanol	100	8	+	>5
reduced Ni	4	5	water	80	16	10.7	>0.8
stabilized Ni	10	2	water	50	6	70	–
stabilized Ni	25	2	water	80	8	78	
copper chromite	4	5	water	80	8	20	+

Table 8–23. Hydration of Nitriles to Amides in Aqueous Solution in the Presence of U–Ni–B

Compound	Weight of sample (g)	Volume of water (ml)	Refluxing time (hr)	Yield of amide (%)	Recovered nitrile (%)	Other product
benzonitrile	5	80	8	78	—	
o–toluonitrile	5.5	80	12	49	—	
p–toluonitrile	7	100	8	63	—	
o–methoxybenzonitrile	10	100	10	33	32	amine, phenolic substance
p–methoxybenzonitrile	10	100	10	65	+	amine
p–hydroxybenzonitrile	4.5	100	5	—	—	metal complex
o–nitrobenzonitrile	5	150	10	54	—	*o*–aminobenzamide (43%)
p–nitrobenzonitrile	5	200	10	50	—	*p*–aminobenzonitrile, metal complex
o–aminobenzonitrile	5	100	5	45	20	metal complex
p–aminobenzonitrile	5	100	5	63	+	metal complex
ethyl *o*–cyanobenzoate	5	150	8	—	40	metal complex
ethyl *p*–cyanobenzoate	5	150	10	—	+	metal complex
p–formylbenzonitrile	5	150	8	—	—	metal complex
mesitylenecarbonitrile	7	100	10	?	~100	metal complex
α–naphthonitrile	7	100	8	19	35.7	amine
2–pyridinecarbonitrile	7	100	10	ca. 40	—	nickel complex
3–pyridinecarbonitrile	7	100	10	89	—	
benzyl cyanide	10	150	10	52	—	amine, phenylacetic acid
benzyl cyanide[a]	10	150	10	83	—	none
acetonitrile	7	100	5	47	—	amine, formic acid, acetic acid, propionic acid
heptanenitrile	3.6[b]	50	5	38	+	
adiponitrile	7	100	10	20	—	unidentified oil, acidic substance

[a] 1 ml of pyridine was added.

[b] U–Ni–B containing 2 g of Ni was used. Other catalysts contained 4 g of Ni.

methanol, or dioxane; in which case, however, the yield of benzamide decreases considerably, and hydrogenation due to the adsorbed hydrogen takes place to a somewhat greater extent to give a larger amount of benzylamine. Moreover, other undesirable side reactions take place depending on the situation. Data on the hydration of benzonitrile in different solvents are illustrated in Table 8–21.

Hydration reactions can be effected as well in the presence of other Urushibara nickels, Urushibara copper, Raney nickel, reduced nickel (prepared from nickel nitrate according to Sabatier's method) or stabilized nickel (nickel catalyst obtained from nickel formate, supported on kieselguhr and stabilized by treatment with carbon dioxide). Data on the hydration of benzonitrile in water or ethanol in the presence of these catalysts are given in Table 8–22.

The best result is secured in the presence of U–Ni–B. U–Ni–A and Raney nickel are also useful, but U–Ni–BA and U–Cu are not so effective and sometimes bring about unexpected side reactions, giving thereby amines or other unidentified compounds. Reduced nickel and stabilized nickel are still less active, and a good yield of benzamide can only be expected with a large excess of catalyst. Hydration in the presence of precipitated nickel or precipitated copper gives only an unknown compound, conceivably a complex of benzylamine and zinc or nickel, and some other unidentifiable oily or crystalline substances.

We see that U–Ni–B enables us to effect the hydration of benzonitrile to benzamide with a good yield. The catalyst is also applicable to the hydration of other nitriles. Aspects of the hydration of a number of substituted benzonitriles and aliphatic nitriles are shown in Table 8–23. Except for a few cases nitriles are hydrated to amides, and the yields are satisfactory (30–80%). In several cases, hydrogenation takes place and amines are obtained as by-products. In other cases, the formation of complexes of nitriles (or intermediate compounds) with the catalyst metal was observed.

Certain aspects of the hydrations of substituted benzonitriles differ according to the kind or position of the substituents. They bear little resemblance to those of acid- or base-catalyzed hydrations.

An ortho effect is clearly displayed and the yields of amides are smaller for ortho-substituted benzonitriles. In particular, mesitylenecarbonitrile is not hydrated and the greatest part is recovered unchanged.

APPENDIX

CATALYTIC ACTIVITY OF PRECIPITATED METALS

A. 1. Novel Catalytic Reduction with Water in the Presence of Precipitated Metals

A number of modifications of the Urushibara catalyst were prepared by digesting precipitated metals with aqueous alkali or acid, and proved to be useful for the catalytic hydrogenation of various organic compounds, the appropriate modification being chosen for the particular purpose. In has been observed, on the other hand, that precipitated metals without digestion by alkali or acid do not catalyze hydrogenation with hydrogen gas under ordinary conditions. It was recently found, however, that various organic compounds, such as olefins, ketones, and nitro compounds, were catalytically reduced when they were refluxed with water in the presence of precipitated nickel.[47] It is noticeable that this reduction is performed by a simple procedure without any hydrogen gas. A unique characteristic of the reduction with precipitated nickel is the use of water as a hydrogen donor, thus making the use of any acid or alkali generally unnecessary. Consequently, the reduction can be performed under practically neutral conditions.

As the reduction proceeds under very mild conditions, the reduction of particular compounds which are sensitive to acid or alkali can be conveniently undertaken. Moreover, this procedure is especially useful in the reduction of a valuable sample which is obtainable only in a small quantity, because it necessitates no special apparatus, thus minimizing the loss of sample.

A. 1. 1. The Reduction of Organic Compounds in the Presence of Precipitated Nickel[47]

The precipitated nickel (abbreviated to ppt-Ni) is easily prepared

Table A-1. The Reaction between Various Organic Compounds and Water in the Presence of Precipitated Nickel

Each run was carried out by refluxing for 12 hr.

Entry No.	Compound	(g)	Nickel content of catalyst (g)	Solvent	(ml)	Reduction product[a]	(%)	Recovered material (%)
1	styrene[b]	10	4	water	100	ethylbenzene	81.4	19.6
2	nitrobenzene[b]	10	4	water	100	aniline	98	–
3	*p*-nitrobiphenyl	1	2	water dioxane	30 10	*p*-aminobiphenyl	80	20
4	*o*-nitrobiphenyl	1	2	water dioxane	30 10	*o*-aminobiphenyl	70	30
5	benzonitrile[c]	10	4	water	100	benzylamine hydrochloride benzamide	90 trace	 +
6	2-pyridinecarbonitrile	0.5	1	water	20	nickel chelate[e] of 2-(aminomethyl)-pyridine	>80	–
7	3-pyridinecarbonitrile	0.5	1	water dioxane	40 20	3-(aminomethyl)pyridine	>80	–
8	4-pyridinecarbonitrile	0.5	1	water dioxane	40 20	4-(aminomethyl)pyridine[d]	>80	–
9	benzaldehyde[b]	10	4	water	100	benzyl alcohol	>90	–
10	*m*-nitrobenzaldehyde	1	2	water dioxane	30 10	*m*-toluidine[d]	>90	+
11	ethyl methyl ketone[b]	10	4	water	100	2-butanol	87	13
12	cyclohexanone[b]	10	4	water	100	cyclohexanol	90	+
13	2-methylcyclohexanone	1	0.4	water	10	2-methylcyclohexanol	42	58
14	menthone	5	2	water dioxane	40 20	*exo*-menthol *endo*-menthol	3 1	>95

15	camphor	5	2	water 40 dioxane 10	*exo*-borneol 2 *endo*-borneol 0.4		>97	
16	ethyl 2-oxocyclopentanecarboxylate	1	0.4	water 10	ethyl 2-hydroxycyclopentanecarboxylate	71		29
17	acetophenone[g]	8	2	water 70	1-phenylethanol ethylbenzene	25 26		49
18	benzophenone[g]	8	2	water 40 dioxane 30	benzhydrol diphenylmethane	31 40		29
19	formylferrocene[g]	0.5	1	water 20 dioxane 10	methylferrocene 1-methyl-2-(ferrocenylmethyl)ferrocene	80 10		—
20	acetylferrocene	0.5	1	water 20 dioxane 10	ethylferrocene	30		60
21	benzoylferrocene	1	2	water 20 dioxane 10	benzylferrocene	<80		—
22	diacetylferrocene	0.5	1	water 20 dioxane 10	diethylferrocene 1-ethyl-1′-acetylferrocene 1-acetyl-1′-(1-hydroxyethyl)ferrocene	10 40 trace	>40	
23	mesityl oxide[b]	10	4	water 100	isobutyl methyl ketone	95[f]		—
24	1,3-diferrocenyl-2-buten-1-one	0.5	1	water 20 dioxane 10	1,3-diferrocenyl-1-butanone	>90		—
25	dypnone	1	2	water 30 dioxane 10	1,3-diphenylbutane	>90		—
26	benzylideneacetone[g]	1	2	water 30 dioxane 10	*n*-butylbenzene 4-phenyl-2-butanone 4-phenyl-2-butanol	6 26 68		—

[a] The yields were calculated from the results of gas chromatographic analysis, except for Entry No. 5. [b] The reaction time was 16 hr. [c] The reaction time was 20 hr. [d] The amine was obtained as the hydrochloride from the reaction mixture by evaporation. [e] The composition of the nickel chelate was found to be $[Ni_2(2\text{-(aminomethyl)pyridine})_5(2\text{-pyridinecarboxylic acid})\ (H_2O)_3Cl]$.
[f] More than 90% even when refluxed for 5 hr. [g] The products were identified by infrared spectra after isolation by gas chromatography.

by adding a hot aqueous solution of nickel chloride to zinc dust (Preparation 2, Chapter 4). After it has been dried under reduced pressure, it is so stable that it can be preserved in the air for a long time. Various organic compounds involving C=C, NO_2, C≡N, and C=O groups were reduced in satisfactory yields when refluxed with water in the presence of ppt-Ni; the results are summarized in Table A–1.

In these reactions, it is noteworthy that water plays a dual role, serving both as a solvent and as a hydrogen donor. Indeed, while water proved to be effective as a hydrogen donor, methanol and ethanol are unsatisfactory. Whereas compounds insoluble in water were reduced only in poor yields, the use of a mixture of dioxane and water facilitated the reaction.

As is seen in Table A–1, ethylenic double bonds were easily hydrogenated in high yields; for example, ethylbenzene was obtained in an 81.4% yield from styrene, and isobutyl methyl ketone in a 95% yield from mesityl oxide. In the reduction of unsaturated ketones, such as mesityl oxide and 1,3-diferrocenyl-2-buten-1-one, the ethylenic double bonds were preferentially hydrogenated, while the carbonyl groups were unaffected.

Ketones were generally reduced to the corresponding secondary alcohols. In some cases a reduction of the carbonyl group to the methylene group was observed, as in the Clemmensen reduction. Thus, dypnone, acetylferrocene, and benzoylferrocene were mostly converted to 1,3-diphenylbutane, ethylferrocene, and benzylferrocene, respectively. The reduction of acetophenone yielded a mixture containing 1-phenylethanol and ethylbenzene, while benzophenone similarly gave benzhydrol and diphenylmethane. Benzylideneacetone gave a more complicated product consisting of 4-phenyl-2-butanol, 4-phenyl-2-butanone, and *n*-butylbenzene. Menthone and camphor were recovered 96% and 97% unchanged, respectively; while only small amounts of the corresponding alcohols were obtained.

Nitriles were predominantly converted to primary amines without the formation of secondary amines, which are often produced as by-products in ordinary catalytic hydrogenations. It is noteworthy that the amines were obtained as their hydrochlorides, the chloride anion presumably being supplied from ppt-Ni. 2-Pyridinecarbonitrile characteristically afforded a metal complex of the amine when treated with water in the presence of ppt-Ni or ppt-Cu, while 3- and 4-pyridinecarbonitrile gave only the corresponding amine hydrochlorides. *m*-Nitrobenzaldehyde was converted to *m*-toluidine by a Clemmensen-type

reduction, wherease benzaldehyde afforded only benzyl alcohol, no appreciable amount of the expected formation of toluene being observed.

Examples of Experimental Procedure:

(*a*) The Reduction of Styrene. A suspension of styrene (10 g) in 100 ml of water was refluxed vigorously in the presence of ppt-Ni containing 4 g of nickel. After the solution had been refluxed for 12 hours, the ppt-Ni was separated by filtration while hot, and washed with water and then with ether. The filtrate and the washings were combined and extracted with ether. The extract was dried over anhydrous magnesium sulfate, and the ether was carefully evaporated away on a water bath. The residue was analyzed by gas chromatography.

(*b*) The Reduction of Benzonitrile. The reaction procedure was almost the same as that described above. After the reaction had been over, the ppt-Ni was filtered off. The filtrate was carefully evaporated to dryness under reduced pressure, and the residue was extracted with ether. The evaporation of the ether extract gave a small quantity of a white solid which was identified as benzamide. A major part of the product, which consisted of a white solid insoluble in ether, was recrystallized from hot water (mp >240°C). It was identified as benzylamine hydrochloride (yield, ca. 90%). The hydrochloride liberated benzylamine when treated with sodium hydroxide solution.

(*c*) The Reduction of Formylferrocene. After the reaction had been conducted in a similar manner, the ppt-Ni was separated and the product was obtained by extraction with ether. The crude product was dissolved in benzene and separated by column chromatography on active alumina (100–200 mesh), using *n*-hexane for elution. A careful evaporation of the yellow elute afforded yellow crystals of methylferrocene (yield, ca. 80%), m.p. 34.9–35.2°C. A successive elution of the column produced a small quantity of a yellow crystalline product, which was assumed to be 1-methyl-2-(ferrocenylmethyl)-ferrocene on the basis of its NMR spectrum.

(*d*) The Reduction of 2-Pyridinecarbonitrile. 2-Pyridinecarbonitrile (0.3 g) and water (10 ml) were refluxed vigorously in the presence of ppt-Ni or ppt-Cu (containing 0.4 g of the catalyst metal) for 10 hours. After the ppt-Ni or ppt-Cu had then been filtered off, the filtrate was carefully evaporated to dryness on a water bath; a green solid was thus obtained. The solid was washed with ether, dissolved in ethanol, and separated by column chromatography on active alumina.

The evaporation of the solvent from the elute gave greenish blue (nickel) or pale blue (copper) needles. These metal complexes were confirmed to be metal chelates of 2-(aminomethyl)pyridine by means of their infrared and ultraviolet spectra.*1)

A. 1. 2. The Relative Activities of Various Precipitated Metals

It has been found[10),13)] that ppt-Ni contains Ni, Zn, ZnO, Zn(OH)Cl, and $Zn(OH)_2$, and that the zinc in ppt-Ni is gradually oxidized to zinc oxide with the progress of the catalytic reaction in the presence of ppt-Ni; thus, the zinc not only acts as a carrier, but also protects the nickel from oxidation.

Since the behavior of zinc was assumed to contribute greatly to the function of ppt-Ni, the effect of a variation in the Zn/Ni ratio on the catalytic reaction was investigated. In Fig. A-1 the correlation is expressed in terms of the yield of cyclohexanol obtained by the reduction of cyclohexanone. As this figure shows, the maximum yield of cyclohexanol was attained by a catalyst whose Zn/Ni ratio was 10. This ratio coincides with that of the ppt-Ni from which the U-Ni catalyst with the highest activity was prepared (see Table 4-1). It

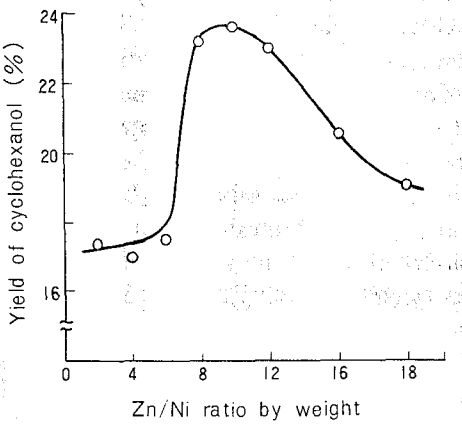

Fig. A-1. The Correlation between the Ratio of Zinc to Nickel and the Yield of Cyclohexanol in Catalytic Reduction with Precipitated Nickel.

Cyclohexanone 1 g; catalyst 0.3 g; water 1 ml
Heated to 111–115°C for 24 hr in a sealed tube

*1) S. Utsuno and K. Sone, *Bull. Chem. Soc. Japan*, **37**, 1038 (1964).

Table A-2. The Relative Activities of Precipitated Metals

Cyclohexanone 1 g; catalyst 0.3 g; water 1 ml
Heated to 111-114°C for 12 hr in a sealed tube

Entry No.	Catalyst	Composition of the reaction product[a] (%)	
		Cyclohexanol	Cyclohexanone
1	ppt-Ni	15.3	84.7
		15.0	85.0
2	ppt-Co	10.0	90.0
3	ppt-Cu	3.5	96.5
4	ppt-Fe	3.4	96.6
5	ppt-Ni,Co	17.7	82.3
6	ppt-Ni,Cu	5.5	94.5
7	ppt-Ni,Fe	15.2	84.8

[a] Products were determined by gas chromatography.

might be concluded from this finding that zinc participates in the reaction by interacting with nickel as well as with water.

From these considerations, other precipitated metals produced by treating a particular metal chlorides with zinc might be expected to be more reactive than the ppt-Ni. Thus, the following precipitated metals were prepared: ppt-Co, ppt-Cu, ppt-Fe, and mixed precipitated metals, such as ppt-Ni,Co; ppt-Ni,Cu; and ppt-Ni,Fe. The relative activities of these precipitated metals were then examined in the reduc-

Table A-3. The Rate Constants of the Reduction of Cyclohexanone at 111.5±2°C, Catalyzed by Various ppt-Metals

Cyclohexanone 0.26 ml; H_2O 0.68 ml; dioxane 0.50 ml; ppt-metal 0.4; in a sealed tube

Catalyst	Rate constant k ($\times 10^2$)(hr^{-1})
ppt-Ni,Co	24.5
ppt-Ni,Fe	17.1
ppt-Ni	14.8
ppt-Co	7.17
ppt-Cu	3.76
ppt-Ni,Cu	1.75
ppt-Fe	0.924

tion of cyclohexanone. The results of representative experiments shown in Table A-2, show the relative activities in the following order: ppt-Ni,Co> ppt-Ni> ppt-Ni,Fe> ppt-Co> ppt-Ni,Cu> ppt-Cu> ppt-Fe. This indicates that the activity of a precipitated metal may be increased by a proper combination of metals.

The rate constant was determined for the reduction of cyclohexanone by water in the presence of various ppt-metals.[48] The results are summarized in Table A-3. The relative activities were found to be in the order: ppt-Ni,Co> ppt-Ni,Fe> ppt-Ni> ppt-Co> ppt-Cu> ppt-Ni,Cu> ppt-Fe. This order is approximately analogous to what is observed by the comparison of the yields of the reduction products.

A. 1. 3. Deuteration with Heavy Water in the Presence of Precipitated Nickel

In order to provide direct evidence for the participation of water as a hydrogen donor, the reduction of benzaldehyde with D_2O in the presence of ppt-Ni was investigated.[48]

The experiment was carried out in a sealed tube by heating benzaldehyde with 99.75% D_2O in the presence of ppt-Ni; deuterated benzyl alcohol was thus obtained in a good yield. However, the attempt to determine the deuterium distribution in the product by the spectroscopic method failed because of the rapid exchange between the D and H in the hydroxyl group due to the moisture in the air. Therefore the product, which was assumed to be a mixture of C_6H_5–CHD–OD and C_6H_5–CD_2–OD, was completely changed to C_6H_5–CHD–OH and C_6H_5–CD_2–OH by vigorous shaking with a large amount of water. The NMR spectrum of the sample thus obtained showed only three sharp singlets, at τ 2.85, 5.60, and 6.35; these singlets are assignable to the phenyl, methylene, and hydroxyl protons, and the intensities correspond to 5, 0.4, and 1 proton respectively. From the proton intensities in the NMR, the ratio between C_6H_5–CHD–OH and C_6H_5–CD_2–OH was estimated to be approximately 40: 60. The IR spectrum of the deuterated alcohols showed an intense band at 2200 cm^{-1}, assignable to the stretching vibration of the CD group. The disappearance of the OD band at 2510 cm^{-1} confirmed the complete exchange of the D in the hydroxyl group for H. The absorption bands in the 650–900 cm^{-1} region, observed in an *n*-hexane solution (0.014 mole/*l*), distinctly showed the presence of a monosubstituted benzene ring, thus demonstrating that no deuterium exchange of ring protons had occurred during the reduction.

These experimental results prove that water acts as a hydrogen donor as well as a solvent in this reduction. The participation of D_2O as a hydrogen donor in the reduction led to the suggestion that this reduction with D_2O would be useful for the synthesis of various deuterated organic compounds as a simpler method than the well-known reduction with $LiAlD_4$ or $NaBD_4$.

A. 1. 4. The Effect of the Amount of Water on the Reduction

Though the presence of water is indispensable for the reduction, the use of an excess of water may be unfavorable because of the low concentration of the reactants. The problem of what constituted an adequate quantity of water for the reduction was examined by using cyclohexanone as a substrate. The reduction reaction of cyclohexanone to cyclohexanol in the presence of ppt-Ni was apparently first-order in the disappearance of the ketone. Typical examples of the apparent first-order rate constants of cyclohexanone in the reactions with various quantities of water are summarized in Table A–4. In order to keep the reaction mixture homogeneous, a given quantity of dioxane was added to the aqueous solution. As is shown in Table A–4, when a comparatively small quantity of water is used the rate constant increases with the increase in the quantity of water. However, the reaction rate gradually decreased when the quantity of water exceeded a certain limit, as had been expected from the decreased concentration of cyclohexanone. The most favorable result was obtained when the H_2O/cyclohexanone mole ratio was about 15:1 (Entry No. 3).

Table A–4. The Effect of Water on the Rate of the Reduction of Cyclohexanone under Refluxing

cyclohexanone 9.8 g (0.1 mole); ppt-Ni 20 g

Entry No.	Water		Dioxane (ml)	Concentration of cyclohexanone (%)	Rate constant k ($\times 10^2$)(hr^{-1})
	ml	mole			
1	16.2	0.9	13	24.8	6.49
2	21.6	1.2	13	21.8	11.30
3	27.0	1.5	15	18.8	13.30
4	32.4	1.8	16	16.7	11.10
5	37.8	2.1	20	14.4	9.00
6	43.2	2.4	20	13.3	9.34

A. 1. 5. The Nature of the Catalytic Reduction with Water in the Presence of Precipitated Metal

The behavior of ppt-Ni contrasts with that of ordinary hydrogenation catalysts. Thus, a rapid decomposition of hydrogen peroxide was observed in the presence of U-Ni, "stabilized nickel", copper chromite, or zinc chromite, but was not observed with ppt-Ni. On the other hand, the effective reduction of the compounds by water, cited in Table A–1, was observed only in the presence of the precipitated metals, whereas U–Ni, Raney nickel, and other hydrogenation catalysts were almost ineffective. The difference between them is reflected in the X-ray diffraction diagrams. The results of X-ray diffraction analysis suggest that the surface of ppt-Ni never consists of nickel itself, but rather is covered with alloy-like layers composed of nickel and zinc, contaminated with OH^- and Cl^-.*1)

X-ray diffraction studies revealed the composition of the ppt-Ni

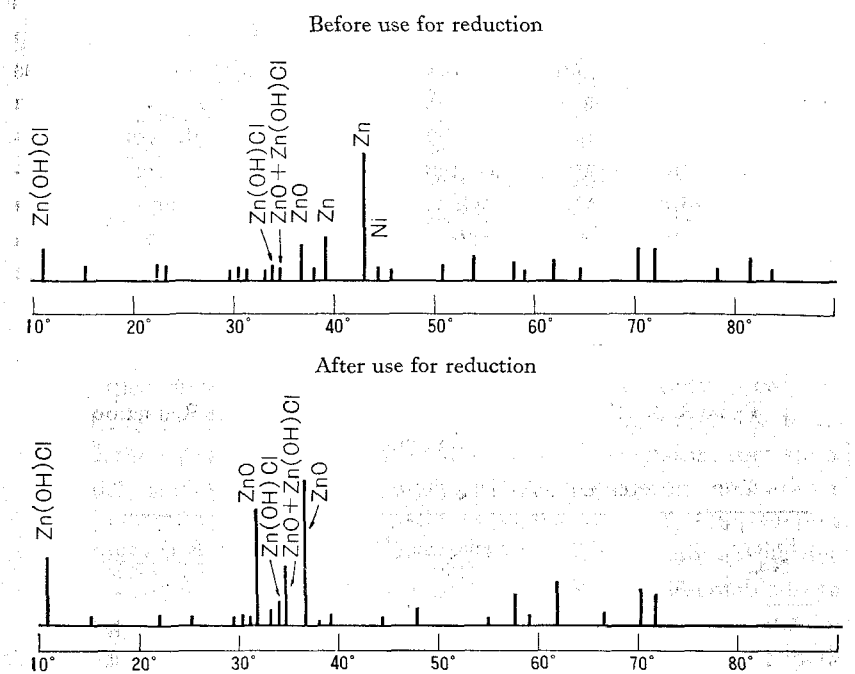

Fig. A–2. X-ray Diffraction Diagrams of ppt-Ni

*1) S. Taira, "Shokubai Kogaku Koza (Catalytic Engineering)," Vol. 10, Chijinshokan & Co., Tokyo (1967), p. 498.

before and after use in reduction by refluxing with water.[48] As is shown in Fig. A-2, the X-ray diffraction diagram of ppt-Ni showed several sharp bands assignable to Zn, Zn(OH)Cl, and ZnO.[13)45] Besides these constituents, ppt-Ni also contains Ni, $ZnCl_2$, and $Zn(OH)_2$, though they are not revealed in the X-ray diffraction diagram. On the other hand, a ppt-Ni recovered after use in reduction by refluxing with water showed a different diffraction diagram, one in which the bands of Zn had disappeared almost completely, while those of ZnO and Zn(OH)Cl were enhanced. This implies that the Zn and $ZnCl_2$ in the ppt-Ni were converted into ZnO, $Zn(OH)_2$, and Zn(OH)Cl in the course of the reaction. It is noteworthy that, when the reaction was carried out in a sodium chloride solution, a remarkable increase in Zn(OH)Cl was observed in the recovered ppt-Ni. From these experimental results, it is concluded that the reaction of water with zinc or zinc chloride is responsible for the supply of hydrogen necessary for hydrogenation.

The increase of ZnO during the reduction reaction suggests that the difference in ionization potentials between a catalyst metal, such as nickel, and zinc may lead to the decomposition of water through a coordination of the water to the zinc. The increase in Zn(OH)Cl may be explained in terms of the participation of $ZnCl_2$, which is necessarily present in ppt-metal. The catalytic behavior of such metal halides as Lewis acids is well known. In a ppt-metal-catalyzed reduction, a donor-acceptor complex may be formed by the combination of water, as a Lewis base, with zinc chloride in the ppt-metal, thus leading to a protonic acid*1; for example:

$$H_2O + ZnCl_2 \longrightarrow \begin{matrix} H \\ H \end{matrix}\!\!>\!O \rightarrow ZnCl_2 \longrightarrow H^+[Zn(OH)Cl_2]^-$$

The formation of Zn(OH)Cl during the reaction may take place through this protonic acid.

Thus the reduction with water in the presence of ppt-metal may be supposed to comprise two steps: the generation of hydrogen or the supply of the hydrogen source from water, and the reduction of organic compounds with the hydrogen.

It has been shown that the generation of hydrogen from water is attributable to the reaction of zinc in the catalyst with water, and also to the difference in ionization potential between zinc and other metals,

*1) H. Meerwein, *Ann. Chem.*, **455**, 227 (1927); *Angew. Chem., Intern. Ed. Engl.*, **5**, 335 (1966).

such as nickel, in the ppt-metal; because the reaction of water with zinc dust alone is extraordinarily slow. Therefore, the amount of hydrogen generated during the reaction depends greatly upon the kind of ppt-metal used.

It has previously been reported that ppt-metal is not useful for ordinary catalytic hydrogenation.[47] However, it was found that cyclohexene can be hydrogenated under ordinary pressure of hydrogen in the presence of ppt-Ni, though the reaction velocity is slow. In this hydrogenation, the activity of the catalyst was found to be dependent on the procedure of its preparation and on the amount of nickel it contained. Therefore, it may be presumed that the behavior of ppt-metals in the reduction step is analogous to that of ordinary hydrogenation catalysts. In this step, metals other than zinc in ppt-metals, such as nickel or cobalt, may play an important part; while zinc may serve for the step of decomposing water.

From this point of view, the activities of several ppt-metals were compared for each of the two steps. The hydrogen gas generated when water was refluxed with ppt-metal alone was introduced into a gas buret and then estimated volumetrically. The volume of hydrogen gas generated when the reaction was carried out in the presence of cyclohexanone under the same conditions was measured in a similar way. Then the volume of hydrogen which had reacted with cyclohexanone was calculated and compared with the amount of cyclohexanol, determined by gas chromatography. The results are listed in Table A-5.

As is seen in the table, the abilities of the ppt-metals to decompose water were found to increase in the order: ppi-Ni<ppt-Cu<ppt-

Table A-5. The Relationship between the Volumes of Hydrogen Generated and Reacted

ppt-metal 0.8 g; H_2O 1.4 ml; dioxane 1 ml; cyclohexanone 0.5 g; reaction time 2.5 hr

Catalyst	Volume of H_2 generated		Hydrogen reacted V_1-V_2 V_3 (ml)	Ratio of reacted hydrogen V_3/V_1 (%)	Yield of cyclohexanol (%)
	in the absence of cyclohexanone V_1 (ml)	in the presence of cyclohexanone V_2 (ml)			
ppt-Ni	90.6	56.5	34.1	38	24
ppt-Cu	120.6	106.4	14.2	12	15
ppt-Ni,Co	138.3	96.4	41.9	30	25
ppt-Ni,Cu	160.5	142.8	17.7	11	9

Ni,Co<ppt-Ni,Cu. This order may be expected if the ability of the ppt-metal to produce hydrogen originates mainly in the difference in ionization potential between the metal in question and zinc.

On the other hand, the ability of each ppt-metal to catalyze the reduction of cyclohexanone was considered to be represented by the ratio of the amount of hydrogen reacting with cyclohexanone to the total amount of hydrogen generated by the decomposition of water. The catalytic activity may also be represented by the yield of cyclohexanol. As is seen in Table A-5, the ratio of the amount of reacting hydrogen was approximately parallel to the yield of cyclohexanol. Thus, the catalytic abilities of the ppt-metals were found to increase in the order: ppt-Ni,Cu<ppt-Cu<ppt-Ni<ppt-Ni,Co. This order coincides with that of the catalytic activities of the corresponding Urushibara catalysts which are prepared from these ppt-metals. The fact suggests that the reducing step of the ppt-metal-catalyzed reaction may be similar to that of ordinary catalytic hydrogenation.

This conclusion is compatible with the results of the observation of the activation energy of the reduction of cyclohexanone with water in the presence of ppt-Ni or ppt-Ni,Co. Table A-6 gives the rate constants of the reaction observed at varied reaction temperatures. The values of the activation energies and the activation entropies were calculated to be 4.0 kcal/mole and −72 e.u./mole, and 7.5 kcal/mole and −59 e.u./mole, respectively, for the reductions catalyzed by ppt-Ni and by ppt-Ni,Co. These values of activation energy resemble that for the catalytic hydrogenation of cyclohexanone with U-Ni-B at room temperature under ordinary pressure, as reported by Nishimura (5.3 kcal/mole).[19] This fact supports the above conclusion that the

Table A-6. The Rate Constants of the Reduction of Cyclohexanone at Various Reaction Temperatures (71-100°C)

cyclohexanone 0.26 ml; water 0.68 ml; dioxane 0.50 ml; ppt-metal 0.40 g

Reaction Temp.		k ($\times 10^2$)(hr^{-1})		log k	
°C	$1/T$ ($\times 10^3$)	ppt-Ni	ppt-Ni,Co	ppt-Ni	ppt-Ni,Co
71.0	2.91	4.40	5.39	−1.35655	−1.28641
80.0	2.83	5.26	7.38	−1.29901	−1.13194
90.0	2.75	5.61	8.78	−1.25104	−1.05651
100.0	2.68	6.90	12.20	−1.16115	−0.91304

function of ppt-Ni as a catalyst is similar to that of ordinary hydrogenation catalysts.

In ppt-metals used as catalysts, active sites for hydrogenation are presumably arranged on the surface of such metals as nickel and cobalt, not on the surface of zinc. This presumption is supported by the facts that, on the one hand, the rate of reduction is dependent on the kind of ppt-metal, and that, on the other hand, the rate stays constant in spite of the consumption of zinc during the reaction.

The fact that the activation energy for ppt-Ni differs from that for ppi-Ni,Co suggests the intervention of a transition state in which cyclohexanone forms a particular complex with the catalyst metal. Thus, the mechanism of the reduction may be considered to be as follows: The coordination of water to zinc or zinc chloride leads to a protonic acid, through which hydrogen is then transferred to active sites for hydrogenation on the surface of nickel or cobalt. The next step is the reaction of cyclohexanone and hydrogen, each of which is adsorbed on the active sites of the catalyst metal in just the same way as in ordinary catalytic hydrogenation.

A. 1. 6. The Acidity and Acid Strength of the Surface of Precipitated Nickel.

It was assumed that the surface of ppt-Ni is covered with alloy-like layers composed of nickel and zinc, accompanied by zinc compouds such as $ZnCl_2$ and Zn(OH)Cl. These zinc compounds may produce protonic acids such as $H^+[Zn(OH)Cl_2]^-$ by reaction with water (see the preceding paragraph). This property of ppt-Ni causes some peculiar phenomena. For instance, the reduction of nitriles in the presence of ppt-Ni produced amine hydrochlorides, while scarcely any free amines were detectable (Table A-1, Entry Nos. 5, 7, and 8).

When the ppt-Ni was soaked in water, a silver nitrate test for chloride ion was negative after 24 hr and only slightly positive after 72 hr. However, when the ppt-Ni was digested in hot water for 72 hr, a distinct deposit of silver chloride was observed in a silver nitrate test of the solution. Consequently, the surface of the ppt-Ni may be assumed to be relatively acidic as a result of coexisting chloride ions, which might participate in the catalytic reaction.

To measure the acidity and acid strength of the surface of ppt-Ni, *n*-butylamine titration*[1] was applied to ppt-Ni in benzene, using

*1) O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955); H. A. Benesi, *J. Amer. Chem. Soc.*, **78**, 5496 (1956).

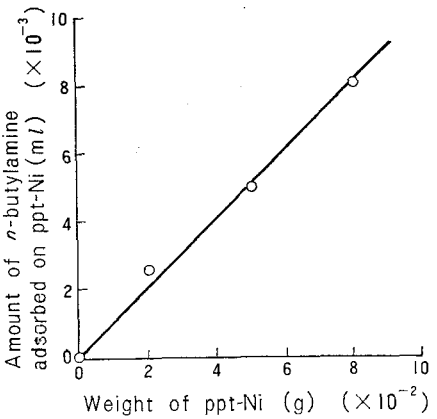

Fig. A–3. *n*-Butylamine Titration of Precipitated Nickel

Methyl Red as an indicator (pK_a 4.8). Though Methyl Red generally changes to a red acidic form when it reacts with an acidic solid, the dark gray color of ppt-Ni makes it impossible to detect any color change in the adsorbed indicator on the solid surface. Therefore, the point of neutralization was determined by noting the change in color on anhydrous magnesium sulfate, which had previously been mixed with ppt-Ni. The relation between the weight of ppt-Ni used and the amounts of *n*-butylamine adsorbed is shown in Fig. A–3. From the slope of the line in Fig. A–3, the acidity of ppt-Ni was calculated to be 1.05×10^{-5} (eq/g) at pK_a 4.8. On the other hand, the acidity of ppt-Ni was nearly zero when Methyl Yellow was used as an indicator (pK_a 3.3). These results imply that the acid strength of the surface is at least more acidic than pK_a 4.8, while the number of acid sites is comparatively small.

A. 2. Catalytic Activity of Precipitated Metals in Hydrogenation at Raised Temperatures

In spite of the earlier observation that ppt-metals are not useful for catalytic hydrogenation unless they are digested with acid or alkali, it was found that they exhibit catalytic activity when they are refluxed in water with various organic compounds.[47] Thereupon, it became an interesting problem to study the possible catalytic activity of ppt-Ni in hydrogenation with hydrogen gas at high temperatures; and in fact, in hydrogenation with hydrogen gas at high temperatures and under

Table A-7. Hydrogenation at Raised Temperatures and Pressures

Entry No.	Compound	Amount of sample (g)	Catalyst	Temperature (°C)	Initial pressure (kg/cm²)	Time (min)	Product and yield (%)	
1	ethyl methyl ketone	14.4	ppt-Ni	22–88	70	70	2-butanol	100
2	ethyl methyl ketone	14.4	U-Ni-B(s)	22–88	70	15	2-butanol	100
3	acetophenone	19.6	ppt-Ni	24–102	50	50	ethylbenzene	54
							1-phenylethanol	43
							unidentified substance	3
4	acetophenone	19.6	U-Ni-B(s)	24–84	50	30	ethylbenzene	1
							1-phenylethanol	94
							unidentified substance	3
5	benzophenone[a]	9.1	ppt-Ni	28–164	50	130	benzylcyclohexane	44
							diphenylmethane	54
6	benzophenone[a]	9.1	U-Ni-B(s)	94–164	50	120	benzylcyclohexane	8
							diphenylmethane	91
7	cyclohexanone	19.6	ppt-Ni	24–114	50	30	cyclohexanol	100
8	cyclohexanone	19.6	U-Ni-B(s)	26–106	50	20	cyclohexanol	100
9	benzaldehyde	10.6	ppt-Ni	24–80	50	25	toluene	65.8
							benzyl alcohol	34.0
10	benzaldehyde	10.6	U-Ni-B(s)	24–88	50	30	toluene	53.0
							benzyl alcohol	28.0
11	benzaldehyde	10.6	ppt-Ni	31	50	140	benzyl alcohol	7.8
12	benzaldehyde	10.6	U-Ni-B(s)	32	50	110	benzyl alcohol	86.1
13	cyclohexene	16.4	ppt-Ni	24–30	50	30	cyclohexane	100
14	cyclohexene	16.4	U-Ni-B(s)	26	50	60	cyclohexane	100
15	styrene	20.8	ppt-Ni	28–92	50	30	ethylbenzene	100
16	styrene	20.8	U-Ni-B(s)	26–40	50	10	ethylbenzene	100
17	benzene	15.6	ppt-Ni	26–176	100	360	cyclohexane	37.0
							unidentified substance	4.0
18	benzene	15.6	U-Ni-B(s)	28–174	100	360	cyclohexane	37.0

[a] In 20 ml of ethanol. Other entries were without solvent.

high hydrogen pressures, ppt-Ni was found to act as a catalyst.*1) The results of the experiments are shown in Table A–7. In these experiments, ppt-Ni was prepared from 10 g of zinc dust in water and 8.1 g of crystalline $NiCl_2 \cdot 6H_2O$, and U–Ni–B(s) by digesting the ppt-Ni with 10% aqueous sodium hydroxide solution. Each catalyst, containing about 2 g of Ni, was washed with water and then with ethanol. The wet catalysts were transferred to an autoclave together with the respective samples.

In the hydrogenation of acetophenone, ppt-Ni gave comparable yields of ethylbenzene and 1-phenylethanol, while U–Ni–B(s) gave nearly exclusively 1-phenylethanol. Benzophenone was hydrogenated to benzylcyclohexane and diphenylmethane in comparable yields by ppt-Ni and to diphenylmethane in major yield by U–Ni–B(s). In the hydrogenation of benzaldehyde at rising temperatures both catalysts gave about the same proportion of toluene and benzyl alcohol, ppt-Ni being slightly more effective than U–Ni–B(s). On the other hand, at a summer room temperature (31–32°C) both catalysts gave only benzyl alcohol, U–Ni–B(s) being much more active than ppt-Ni. Cyclohexene was exceptionally easily hydrogenated at room temperature with either catalyst. With styrene and benzene, ppt-Ni and U–Ni–B(s) gave similar results.

The activity of ppt-Ni in the reduction of cyclohexanone to cyclohexanol was tested at varied temperatures but under the same initial pressure of 50 kg/cm². The results are shown in Table A–8. The table indicates that the catalytic activity of ppt-Ni depends greatly on

Table A–8. Reduction of Cyclohexanone to Cyclohexanol at Various Temperatures

Cyclohexanone: 19.6 g without solvent
ppt-Ni: containing about 2 g of Ni
Initial pressure: 50 kg/cm²

Entry No.	Temperature (°C)	Reaction time (min)	Recovered cyclohexanone (%)
1	24	60	100
2	50	60	59
3	70	60	0

*1) Unpublished data from S. Ishiwata, M. Kajitani, H. Tomoda, and Y. Urushibara of Sophia University.

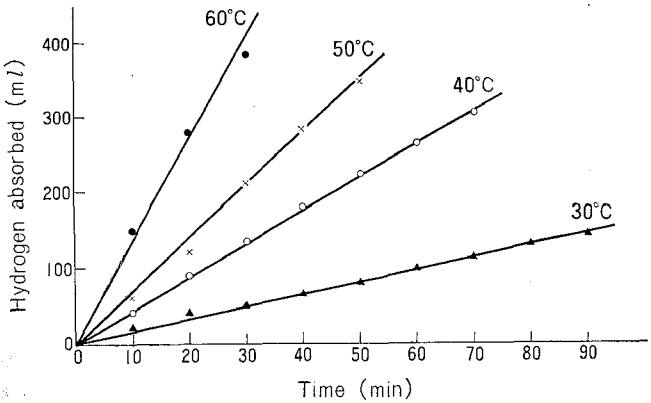

Fig. A–4. Initial Rates of Hydrogen Absorption at Various Temperatures

Cyclohexanone: 2 g in 20 ml of ethanol
ppt-Ni: containing about 2 g of Ni

the temperature and does not appear at ordinary temperatures, even under high pressure.

Next, hydrogenation with ppt-Ni at various temperatures but under ordinary pressure was attempted. Fig. A–4 shows the initial absorption rate of hydrogen when 2 g of cyclohexanone in 20 ml of ethanol was shaken with hydrogen in the presence of ppt-Ni containing about 2 g of Ni, the sum of the pressures of the hydrogen and the ethanol vapor at the respective temperatures being about 1 atm. The effect of the temperature is again remarkable. As practically no hydrogen was absorbed at 20°C, ppt-Ni does not function as a catalyst at this temperature, in contrast to the high activity of finished U–Ni–B. As the apparent heat of activation of the reduction of cyclohexanone to cyclohexanol in the presence of ppt-Ni, a value of 15.56 kcal/mole was calculated from the data given in Fig. A–4, while a value of 5.95 kcal/mole was obtained for the reduction in the presence of U–Ni–B(s).

Then the question arose as to whether preliminary heating of ppt-Ni with either ethanol, cyclohexanone, or cyclohexanol, without hydrogen, might give a catalyst active at ordinary temperatures. It was found, however, that ppt-Ni, after being heated with any one of these, is almost entirely inactive as a catalyst in the reduction of cyclohexanone with hydrogen at ordinary temperatures. Heating of ppt-Ni with hydrogen

but without reducible substances will give further information on the nature of the catalysis by ppt-Ni at high temperatures.

Another problem is the role of zinc, which is present in a large excess in ppt-Ni. The color of ppt-Ni turns from black to gray after use. Further, it was revealed by an X-ray diffraction study that the metallic zinc contained in ppt-Ni before use in hydrogenation has disappeared and changed into zinc oxide after use (Entry No. 7 of Table A–7). A similar phenomenon was observed by Sakai *et al.* in hydrogenation by refluxing with water in the presence of ppt-Ni (see Fig. A–2).[48] There, the role of zinc was considered to consist in the decomposition of water to produce hydrogen for hydrogenation catalayzed by nickel without hydrogen gas. In the present case, however, hydrogen gas is used instead of water; and although the source of the oxygen combined into zinc oxide has not yet been determined, water adsorbed on ppt-Ni and ethanol remaining in considerable amounts after being used to displace water are possible oxygen suppliers. Cyclohexanone is quantitatively reduced to cyclohexanol, and thus these could not supply oxygen. If the oxygen was supplied by the adsorbed water, a course similar to that observed in hydrogenation by refluxing substances with water in the presence of ppt-Ni might occur. However, it is certain that the hydrogen from water, if any, constitutes only a minor proportion of the hydrogen added to cyclohexanone; for a reasonable amount of hydrogen gas was absorbed, and reduction of 19.6 g (0.2 mole) of cyclohexanone to cyclohexanol in a 100% yield requires 0.2 mole of hydrogen corresponding to 3.6 g (0.2 mole) of water, and such a large amount of water can not be considered to have remained adsorbed on ppt-Ni after washing with ethanol. The fate of the other moiety of either possible substance supplying the oxygen is also obscure.

The nature of the catalysis by ppt-Ni at raised temperatures is not yet clearly understood; but in practice its selectivity, probably arising from its neutrality, or slight acidity due to the hydrolysis of adhering chlorides, against the alkalinity of finished U–Ni–B(s), can be utilized in some cases. In view of the great value of the apparent energy of activation for the reduction of cyclohexanone to cyclohexanol in the presence of ppt-Ni and the much smaller value for U–Ni–B(s), it may be said that the finished catalyst possesses far better catalytic qualities than the precipitated metal, which at ordinary temperatures hardly functions as a catalyst at all.

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